TÉCNICO LISBOA

# Green Hydrogen and Oxygen Economy developments in Portugal


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## ABSTRACT

In order to decarbonize the energy industry, green hydrogen will have a crucial role. However, water electrolysis is still highly capital intensive. Currently, the most predominant and cost-effective process to produce hydrogen is Steam Methane Reforming. The aim of this work is to study the competitiveness of the economic activities that consume oxygen in Portugal, which is co-produced during the electrolysis process. Amongst all these industries, the glass production was reported to be the largest industry in Portugal. Also, given that medical oxygen has a high market value, the consumption of medical oxygen in Portugal and Spain was characterized and quantified. In fact, the hospitals in Portugal with the highest annual oxygen demand have proven to be in Lisbon, Coimbra and Porto. Another key insight of this study is the medical oxygen demand for home care treatments, with an increased market value due to the pressurized cylinders in which oxygen is transported and stored.

Furthermore, the economic activities that consume Hydrogen were characterized, as well as the scenario for future consumption. The most important sector in Portugal is Oil refining, in Sines, having the highest hydrogen demand amongst all other described industries. Another important insight of this work is the comparison between both Alkaline and PEM electrolysers, where Alkaline electrolysers have the highest maturity level with an estimated CAPEX value of 900 €/kW. In fact, all techno-economic calculations presented throughout this work are based on an alkaline electrolyser. Also, this study evaluates in which Portuguese geographical locations would it be more promising to install electrolysers plants, according to both hydrogen and oxygen industry consumers nearby. As it will be shown, the oxygen price will influence significantly the calculations of CAPEX and OPEX, NPV, IRR and payback period of the studied subsystems, contributing ultimately to the economic viability of the electrolysis process.

Although significant financial benefits were observed when selling oxygen as a by-product, government funds and loans are crucial to reduce the green hydrogen selling price, thus rapidly increasing market penetration.


**Key-words:** energy; Alkaline water electrolysis; oxygen; hydrogen; medical oxygen

## RESUMO

Com o propósito de descarbonizar a indústria energética, o hidrogénio verde terá um papel essencial. No entanto, o processo da eletrólise da água continua a exigir um investimento inicial bastante elevado. Atualmente, o processo mais predominante e rentável para produzir hidrogénio (cinzento) continua a ser através do gás natural. O objetivo desta tese é estudar a competitividade das indústrias consumidoras de oxigénio em Portugal, produzido como subproduto durante a eletrólise. De todas estas indústrias, destaca-se o fabrico de vidro, pelo facto de ser a maior indústria em Portugal, bem como pela quantidade de oxigénio que necessita. Além disso, dado que o oxigénio hospitalar tem um elevado valor de mercado, o consumo de oxigénio médico em Portugal e Espanha foi igualmente quantificado. De facto, os hospitais em Portugal com o maior consumo anual de oxigénio são os de Lisboa, Coimbra e Porto. Um outro aspeto importante deste estudo é o consumo de oxigénio médico para tratamentos domiciliários, sendo que possuem um maior valor de mercado devido às garrafas pressurizadas nas quais o oxigénio é transportado e armazenado.

As atividades consumidoras de Hidrogénio foram igualmente estudadas, bem como o seu cenário futuro. O sector mais importante em Portugal é a refinação de petróleo, em Sines, que representa o maior consumo anual de hidrogénio industrial. Este projeto compara também a tecnologia dos eletrolisadores Alcalinos e PEM, de onde se estimou que os alcalinos representavam um valor de CAPEX de 900 €/kW. De facto, todos os cálculos tecno-económicos apresentados ao longo deste trabalho são baseados na tecnologia alcalina. Além disso, este estudo avalia em que localizações geográficas portuguesas seria mais promissor instalar eletrolisadores, com base nos consumidores de hidrogénio e oxigénio na periferia dessas regiões. Como será demonstrado, o preço do oxigénio influenciará significativamente os cálculos de económicos realizados, contribuindo em última análise para a viabilidade económica da tecnologia em causa.

Por fim, apesar de terem sido observados benefícios financeiros significativos na venda de oxigénio como subproduto, fundos e empréstimos serão cruciais a curto prazo, de modo a reduzir o preço de venda do hidrogénio verde, aumentando assim rapidamente a penetração no mercado.


**Palavras-chave:** energia; eletrólise alcalina da água, oxigénio, hidrogénio, oxigénio médico

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# GLOSSARY

**AEC** Alkaline Electrolysis Cell

**AOP** Advanced Oxidation Process

**ASU** Air Separation Unit

**BEKP** Bleached Eucalyptus Kraft Pulp

**BOD** Biochemical Oxygen Demand

**CAPEX** Capital Expenditures

**CASK** Cost of available seat kilometre

**CCGT** Combined Cycle Gas Turbine

**CCS** Carbon Capture and Storage

**COD** Chemical Oxygen Demand

**ECF** Elemental Chlorine Free

**IGCC** Integrated Gasification Combined Cycle

**IRR** Internal Rate of Return

**MAP** Modified Atmosphere Packaging

**MIBEL** IberinaIberian Electricity Market

**MIEC** Mixed ionic electronic conducting

**MSW** Municipal Solid Waste

**NECP** National Energy and Climate Plan

**NPV** Net present Value

**OBF** Oxygen Blast Furnace

**OPEX** Operational Expenditures

**PBP** Payback Period

**PEM** Proton Exchange Membrane

**PSA** Pressure Swing absorption

**PtG** Power to Gas

**PtL** Power to Liquid

**RES** Renewable Energy Source

**RFG** Recirculated Flue Gas

**SCWO** Supercritical Water Oxidation

**SMR** Steam Methane Reforming

**SNG** Synthetic Natural Gas

**SOEC** Solid Oxide Electrolysis Cell

**SPE** Solid Polymer Electrolyte

**TCF** Totally Chlorine Free

**TSA** Temperature Swing Absorption

**ULCOS** Ultra Low $CO_2$ Steel Making

**VSA** Vacuum Swing Absorption

# 1 INTRODUCTION

## 1.1 Motivation

The National Energy and Climate Plan (NECP) expects to reach the economy decarbonization by promoting energy transition, in agreement with the European legislation and points to the next decade as decisive to the achievement of these goals.

Portugal targets are extremely ambitious, with their achievement depending substantially on the investment capacity collected by the renewable sector.

The NECP responds to the European political framework, which establishes goals regarding primary energy consumption, the incorporation of renewables in the final gross energy consumption and electrical interconnections, and naturally the reduction of greenhouse gas emissions. In order to accomplish these objectives, the renewable energy installed capacity growth is intended to double from 2018 to 2030.

With respect to the renewable electricity share in Portugal, during 2019, this represented 55.2% of the national demand, led by the wind technology, with 27%, followed by hydro technology with a normalized share of 20 %, solar photovoltaics with 2.2%, bioenergy with 5.7% and geothermal with 0.3% [1] (figure 1).

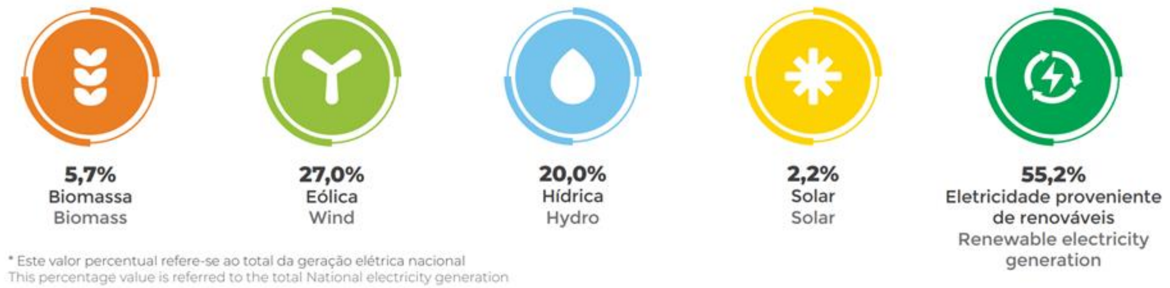


Figure 1 - Contribution in the electricity generation in 2019 [1]

These percentage shares, which are continuously increasing, represent endless benefits regarding social impact, the economy and the environment, with the following values calculated for 2019: Savings of 743 million € in fossil fuel imports; 15 million tonnes of avoided $CO_2$ emissions and 374 million € avoided in $CO_2$ emission allowances [1].

Furthermore, the Portuguese renewable installed capacity has been increasing with a yearly average growth rate of 6% since 2005, while the fossil fuel installed capacity has reduced over the years since 2011 [1] (figure 2).

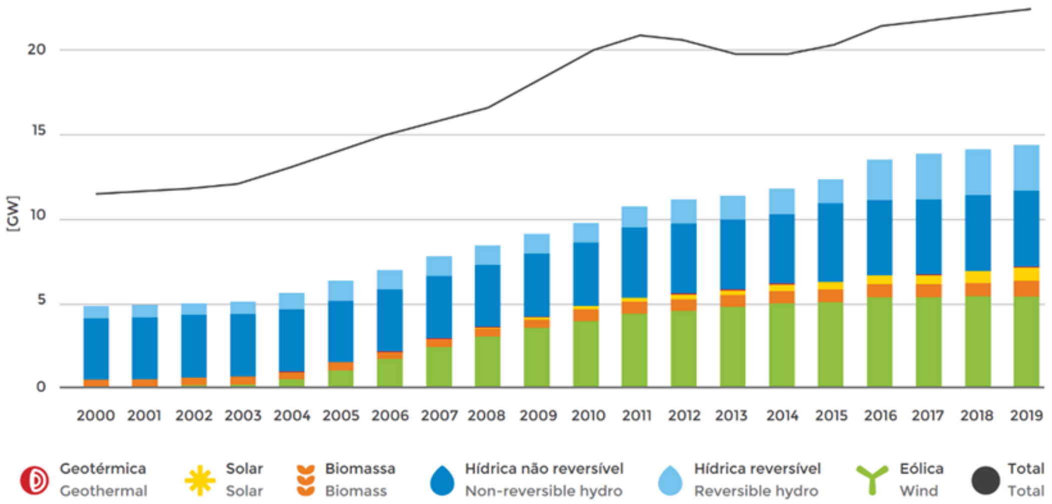


Figure 2 - Installed capacity by electricity generation source [1]

Between 1 of January and 31 of December 2020, the electricity system of mainland Portugal registered electricity imports of 6 397 GWh and exports of 4 942 GWh, resulting in an import balance of 1 455 GWh, which is 57% lower than the import balance verified in the exact same period in the year of 2019 [2].

The percentage of renewable generation in 2020 increased by 5.6% compared to 2019 whereas the total electricity generation growth (in GWh) was 1.1% [2].

Furthermore, throughout the year of 2020, there was an average hourly price in the Iberian Electricity Market (MIBEL) in Portugal of 34.1 €/MWh, which represents a cutback of 29% compared to the same period last year. In fact, such value corresponds to the lowest average price ever registered in the Iberian Electricity Market. This price reduction took effect in all countries in the European market, partially due to the electricity consumption drop during the COVID-19 Pandemic [2].

In 2030, it is estimated that RES will be responsible for more than 28,000 MW installed. In terms of sectors distribution, it is estimated that the solar will account for the largest contribution (9,600 MW, considering centralized, decentralized photovoltaic energy and concentrated thermal solar), followed by wind (9,200 MW) and hydro, which will be responsible for 8,700 MW. Hence, the installed capacity in the Portugal will evolve towards a well-balanced distribution among these renewable energy sources [3] (figure 3).

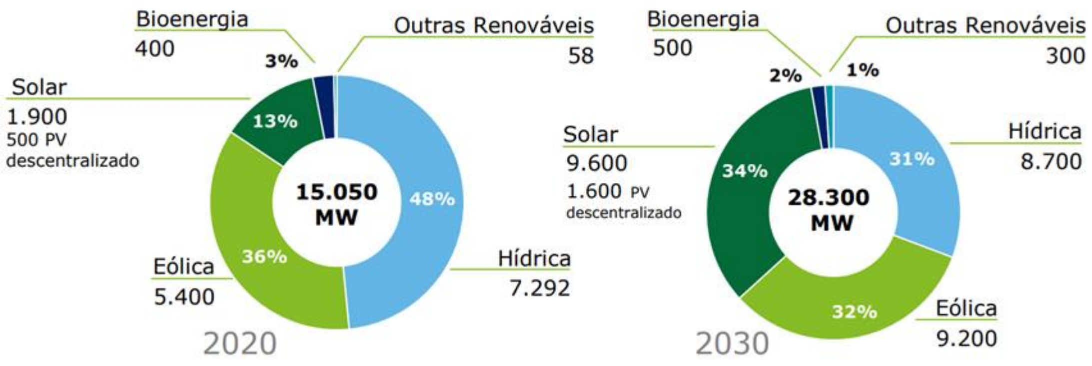


Figure 3 - RES installed capacity distribution in 2020 and 2030 (MW) [3]

The evolution of renewable installed capacity in Portugal will enable the renewable electricity production in Portugal to rise from 25,514 GWh, in 2015, to 66,528 GWh, in 2030. Contrariwise, non-renewable production is expected to decrease by 61% from 28,910 GWh in 2015 to 11,191 GWh in 2030 [3] (figure 4). In terms of the total amount of energy produced, it is expected an increase of more than 40% between 2015 and 2030, which is also show in the figure below.

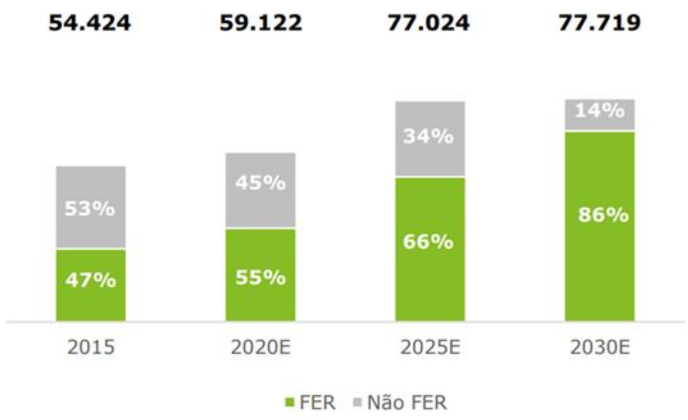


Figure 4 - Estimation of the Electricity production evolution in Portugal (GWh) [3]

In conclusion, Portugal has the opportunity to become a leading country in terms of renewable energy production. In fact, this study will analyse not only the importance in investing in green hydrogen production from water electrolysis process, but also focus on the possibility of reselling Oxygen as by-product. As renewable energy shares in Portugal increase, it is imperative to adapt traditional fossil fuels powerplants to power to gas (PtG) or power to liquid (PtL) options in order to better tackle wind and solar intermittency.

The ultimate goal is to continually reduce Portugal's imports balance or even in a more optimistic scenario, become an electricity exporting country in Europe.

## 1.2 Objectives

The objective of this thesis is to study the competitiveness of the economic activities that consume oxygen in Portugal, which is produced as a by-product during the electrolysis process. In addition, this study attempts to identify the best locations for installing alkaline electrolysers, based on hydrogen and oxygen consumers nearby. The ultimate goal is to present an optimistic scenario where these gases were to be delivered via a direct line and consumed in real time by interested industries, thus avoiding compression and storage costs and becoming very cost attractive.

## 1.3 Structure of the thesis

This work is essentially divided in four main sections, the Introduction, which includes the motivation and objectives of this thesis, as well as the structure explanation, the Literature review, Results and discussion and the Conclusions reached.

The Literature Review includes several industries which consume oxygen, focussing on their maturity level, economic value and also possibility for becoming more sustainable and reducing carbon emissions. Based on reference oxygen demand values for all industries analysed, calculations and estimations were performed for Portugal, with the aim of quantifying the sectors with the highest oxygen demand. Current hydrogen applications were also analysed and revised, although with less detail since the major focus of this work was to assess the oxygen value.

The Results and discussion section include two different studies. The first one, is based on quantifying gases consumption for several industries and understand where geographically are these industries located, by using Excel´s tool 3D Maps for Portugal. The second part of this section is based on a sensitive analysis for the instalment of a reference 1MW Alkaline electrolyser in one of the locations proposed, including oxygen selling in the revenues. The electrolyser was assumed to be powered by solar electricity, which could be delivered by an already proprietary PV plant or a purchased one, for which extra costs have to be considered.

Finally, the main findings and conclusions from this work are presented and discussed, as well as providing some future work recommendations.

# 2 Literature review

## 2.1 Cost evaluation of Green Energy in Portugal

Renewable energy sources are becoming more competitive with fossil fuels, with a tendency to increase its penetration in the market. In fact, green energy cost is expected to continue to decrease in the future, as wind and solar grow into more mature technologies.

In Portugal such tendency is noticeable. Cost related to solar PV installation have reduced by 90% since 2010[4]. Silicon solar panels price have dropped from 2€/W to around 0.20€/W. Therefore, in terms of energy cost, currently solar energy is between 1.2 and 1.6 €/Wh [5]. Solar energy is currently amongst the cheapest forms of producing electricity, partly due to the effect of scale economies. The majority of solar modules in the market are produced from crystalline silicon solar cells, which have also suffered a significant price variation over the years. In 2010, polycrystalline silicon cells used to cost around 80€/kg, while in 2019 the average market price was slightly above 8€/kg [4].

Such difference in the polycrystalline silicon cells market price represents a final cost reduction of 10 times in just over a 9 years period. This radical drop is associated with the developments made regarding the advancements accomplished in nanostructured silicon-based layers [6]. Moreover, improvements have been made relatively to layer voltage loss and energy conversion efficiency. Technology has advanced from a direct contact of the silicon wafer and metal into a more efficient system by introducing buffer layers between the semiconductor and the metal. In fact, adding a slender silicon oxide buffer layer reinforced with semi-insulating poly-silicon, reduced significantly voltage losses in the solar panel. In order to further increase transparency, ongoing researches are being carried out to assess poly-silicon replacement for nanostructured layers. Promising results have been obtained regarding a mixed-phase layer consisting of an amorphous SiOx matrix reinforced with silicon fibre, known as nanocrystalline silicon oxide (nc-SiOx) layer [6]. Nevertheless, monocrystalline cells are currently the most predominant material amongst solar panels, due to its enhanced efficiency.

In the wind sector, it is also noteworthy to analyse the market price variation. According to the European Wind Energy Association, the current price for onshore wind turbines is around 105 €/MWh [7]. Comparing to conventional fossil fuel sources, wind is already more competitive. In fact, for natural gas applications, the current market price is 164 €/MWh. For the case of coal powerplants, the price is 233 €/MWh [7]. Despite coal and natural gas being more mature technologies, $CO_2$ emission allowances affect drastically the final energy cost. For the offshore technology, the costs associated are higher, since it requires more complex infrastructure.

Nevertheless, as climate change concerns arises, and carbon licenses become more regulated, fossil fuel sources will develop into very expensive electricity sources. Contrarily, with the correct incentives in energy and fiscal national policies related to the investment in renewable energy sources, wind and solar will continue to decrease its market price, making them highly competitive.

## 2.2 General industry applications of Oxygen

Oxygen is widely used in many industries in Portugal such as chemical, waste and water management, glass, hospital care, metal fabrication, paper bleaching and also petrochemical.

In fact, as it will be shown in this study, oxygen price for industrial applications will be around 100€/tonne, varying according to mass production and also its penetration in the market [8].

Oxygen improves a significant number of petrochemical processes: mainly oxidation reactions such as the production of ethylene and propylene oxide, for methanol production, and also for power generation and fuel production purposes, namely, oxyfuel combustion process, coal gasification systems as well as syngas production. Moreover, significant improvements are being made regarding oxygen production, using advanced membrane-based separation processes instead of cryogenic air separation, enabling zero Nitrogen Oxide ($NO_x$) emissions combustion.

Presently, it is still more economical to produce hydrogen with fossil-fuelled based technologies such as steam methane reforming, in comparison to alkaline water electrolysis. The hydrogen production cost via electrolysis is extremely high because of the large amount of investment involved and also due to the quantity of electricity needed to power the electrolyser. Nevertheless, technological improvements in electrolysis technologies and the continuous cost reduction of renewable energy resources over the years, increase of methane price and increase of $CO_2$ taxation, could make the production of hydrogen by electrolysis very engaging for the future. Another factor which would influence drastically the final cost would be the possibility of the oxygen obtained as by-product being sold afterwards for further applications.

For large applications, it is even more imperative oxygen utilization, since also a large amount of hydrogen should be produced from renewable resources via electrolysis process. For instance, a 1MW Alkaline electrolyser with 70% efficiency, corresponding to 178 kg/h of $H_2O$, originates 20 kg/h of hydrogen and 158 kg/h of oxygen with a ratio of 8 kg of $O_2$/kg of $H_2$, which is stored as a by-product for sale [9]. In this situation, the by-product oxygen should be completely put to use, due to its unique and important applications for industrial purpose. Furthermore, the adequate utilization of oxygen would result in major improvements in the overall energy efficiency of industrial processes related to glass melting and iron making. For this reason, it seems much more reasonable to explore its possible large-scale utilization, despite the fact that oxygen from water electrolysis can be harmlessly vented into the atmosphere [10](figure 5).

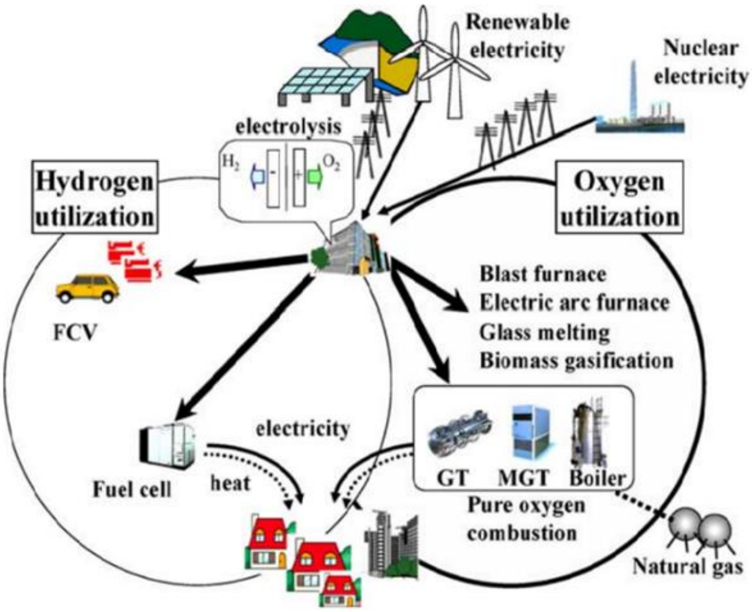


Figure 5 - Conceptual diagram of simultaneous utilization of hydrogen and by-product oxygen [10]

Countless industrial applications with high energy consumption could reduce the amount of heat lost to the atmosphere by about 66%, by using oxygen-enriched combustion air [10]. Demand for oxygen is expanding in processes such as glass melting and electric furnaces, as well as waste water and in treatment of municipal solid waste (MSW), due to political concern amongst European countries regarding environment sustainability. In addition, the utilization of by-product oxygen could even reduce the amount of electricity consumed in cryogenic air separation and pressure swing absorption (PSA), which are currently the most traditional air-separation processes. By-product oxygen produced and oxygen demand should have an equitable relation, in order to maximize de water electrolysis process and avoid unnecessary oxygen vented. In terms of market price, a recent research estimates oxygen production via PSA and cryogenic separation at 100 to 120 €/tonne of $O_2$ [11].

### 2.2.1 Methanol

The strong investment made in renewable sources of energy such as solar and wind, has brought some controversy in Portugal regarding combined cycle power plants. Some of these consequences are causing critical operation conditions, forcing power plants to function at lower efficiencies and also frequent start-up/shutdown, which naturally impacts their lifetime. In fact, coal driven powerplants in Portugal are already being replaced by more sustainable solutions, with already ongoing projects regarding power to hydrogen and power to ammonia technologies [12]. In order to tackle such concerns, the power-to-liquid systems are also being studied for the future energy scenarios. Similar to power to gas solutions, such technology will also compensate for the renewable energy source intermittency, securing stability in the national electrical grid. Furthermore, it would also have a positive impact on the shut downs which affect traditional power plants efficiencies. In comparison with PtG, liquid solutions present less implementation barriers regarding not only transportation but also safety and infrastructure concerns.

One of the most encouraging products to be used in PtL systems is in fact methanol (formula $CH_3$OH), with a melting and boiling point of −97.6 °C and 64.7 °C, respectively, and a density of 20.1 MJ/kg [8]. Methanol, which is in liquid state at atmospheric condition, presents interesting combustion properties, in particular regarding its octane number. In comparison with gasoline (95 octane number), methanol presents an octane number of 108, enabling higher compression ratio, thus a superior combustion efficiency [8].

Methanol is also a key component in biodiesel, which is a renewable fuel that can be used as an additive of conventional diesel fuel. In fact, the Portuguese government will compel energy companies to respect a physical incorporation of 6.75% of biodiesel in the diesel fuel, as a result of the increasingly rigorous emissions regulations.

Researchers are also studying the use of methanol as a clean-burning marine fuel. Nowadays, methanol for industrial purposes is mostly produced from natural gas by steam reforming or coal gasification. The resulting syngas of the methanol synthesis (CO and $H_2$ or $CO_2$ and $3H_2$) is composed by CO, $CO_2$ and $H_2$. However, such process is responsible for large emission amounts of carbon dioxide, releasing into the atmosphere about 0.6 to 1.5 tons of $CO_2$ for each ton of methanol produced [8].

#### 2.2.1.1 Methanol Production plant from CCS

A recent work was performed in Germany [8] with reference to the E.U.Mef$CO_2$ project (consists in obtaining methanol fuel from carbon dioxide sequestration), which was approved by the Horizon 2020 EU Research and Innovation program [13]. The main goal of this project was to produce synthesized methanol with minimum carbon dioxide emissions. In order to do so, the carbon dioxide emitted from the traditional powerplant is efficiently captured and stored. Subsequently, it reacts with hydrogen, which is produced from water electrolysis powered by renewable energy surplus.

For this particular study, a reference powerplant was chosen with a flue gas mass flow rate of 700 kg/h and containing 17% of $CO_2$ on a mass basis [8]. Also, an amine-based CCS system was considered.

In fact, not only does this process represent a sustainable solution for the methanol production by it also drastically reduces fossil fuel emissions. The reaction which represents the synthesized methanol production is given by:

$$3H_2 + CO_2 \rightarrow CH_3OH + H_2O \qquad (1)$$

Note that the catalysis occurs with temperature and pressure intervals of 250–300 °C and 50–100 bar, respectively on CuO/ZnO/$Al_2O_3$ as catalyzer [8].

The German economic scenario was chosen as a reference case. However, such study can be easily scaled into Portugal, since both countries have the same currency. Also, as previously shown in this work, renewable energy installed capacity in Portugal is also increasing, making this country a good scenario for such power plant application. The figure below represents the overall share from renewable energy sources in 2019 as well as the target 2020. In fact, in terms of gross final energy consumption percentage, Portugal recorded a 50% larger value compared to Germany [14](figure 6).

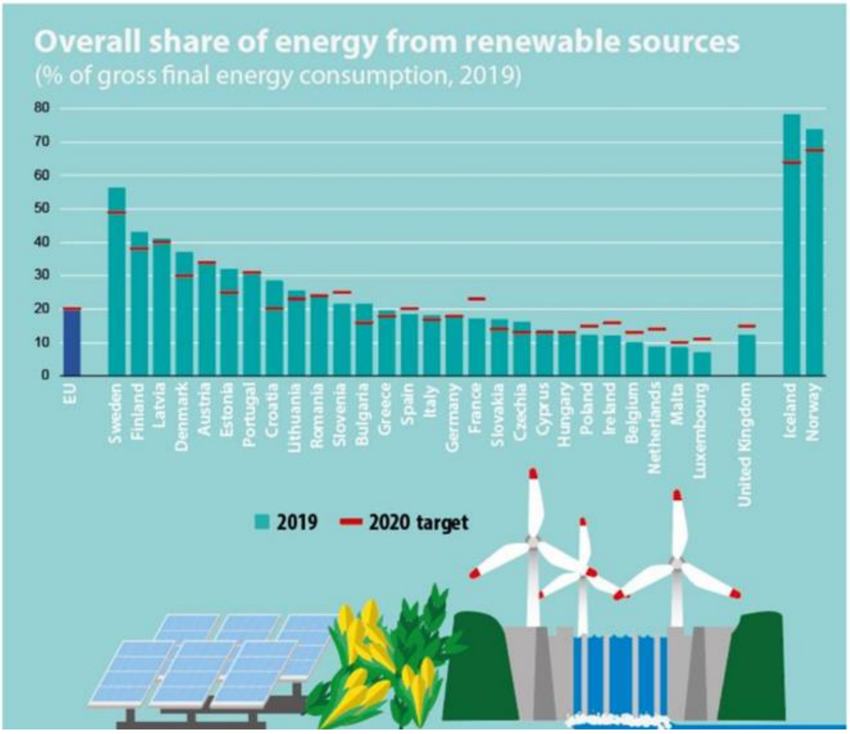


Figure 6 - Overall share from renewable energy sources in 2019 [14]

This process to obtain methanol consists in 3 major steps:

- A PEM electrolyser, where $H_2O$ is separated into $H_2$ and $O_2$: hydrogen is used in the methanol synthesis, whilst oxygen is directly sold for industry purposes. Note that as previously mentioned, the amount of oxygen co-produced is around 8 kg for each kg of hydrogen produced).

- Carbon Capture Sequestration (CCS) section: the amine-based CCS is connected to a coal-fired power plant and sequestrates $CO_2$ for methanol synthesis;

- Methanol reactor, where $CH_3OH$ is synthesized, after the reactants $H_2$and $CO_2$ are compressed.

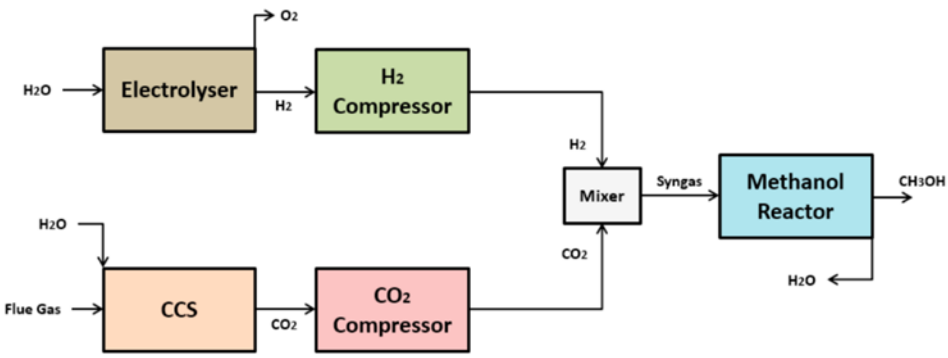


Figure 7 - Synthesized Methanol production plant layout [11]

A 1MW PEM electrolyser with a 68% efficiency produces about 19 kg/h of hydrogen and 151 kg/h of oxygen. In order for the methanol reaction to occur, around 140 kg/h of $CO_2$ are sequestrated by the CCS system [8].

Table 1 - Main technical parameters considered [8]

| | |
|---|---|
| PEM Electrolyser | |
| Electrical consumption | 5.2 kWh/Nm$^3$ di $H_2$ |
| Pressure | 30 bar |
| Temperature | 80 °C |
| Efficiency | 68% |
| Carbon Capture system | |
| Treatment kind | Amines (MEA) (30%) |
| Flue gases inlet T[°C] and p[bar] | 40 °C, 2 bar |
| Thermal energy consumption per ton of $CO_2$ | 3 $GJ_{th}/kgCO_2$ |
| $CO_2$ outlet temperature[°C] pressure[bar] | 40 °C, 2 bar |
| $CO_2$ capture rate | 90% |
| Methanol Reactor | |
| Working Pressure | 80 bar |
| Temperature | 240 °C |
| Recirculation factor of unreacted syngas | 0.85 |
| Conversion efficiency | 96% |
| Molar $H_2$:$CO_2$ ratio | 3:1 |
| Compressor | |
| Isentropic efficiency | 86% |
| Mechanical efficiency | 99% |

Oxygen selling price is assumed to be between 100 €/tonne and 150 €/tonne [8], [11], considering industrial market value. Nevertheless, medical industry has even higher market value. This represents a very attractive application of electrolysis by-product oxygen, especially for large application scales. Moreover, studies show that, in the majority of the cases, the purity of oxygen produced by electrolysers is sufficient for industrial applications, therefore not requiring further purification treatments. Regarding the methanol selling price, the current average market value in European countries is around 400 €/tonne [11]. Note, however, that methanol market value is expected to rise in the next years, due to its range of sustainable applications and also the important role it might have in the energy transition period.

Another factor that weighs in an economical evaluation is the electrical energy cost, which is strongly affected by the country where the methanol powerplant is to be implemented. Comparing Germany with the Portuguese scenario, it can be seen that the electrical energy cost is very similar in both countries, being around 33 €/MWh in Germany [11] and 34,1 €/MWh in the Iberian Electricity Market (2020)[2].

Considering a minimum value of 100 €/tonne for the average industrial oxygen price, a compelling impact can be seen in the plant economic evaluation. In fact, the results obtained when selling oxygen for further applications decrease the overall methanol selling price when compared to oxygen being vent to the atmosphere [8].

D. Bellotti, M. Rivarolo, L. Magistri also concluded that the oxygen sale represented 37% of the total revenues of the powerplant and it played a crucial role in the economic feasibility of the plant [11]. For this reason, the impact of an increase in the oxygen selling price up to 200 €/ton was further investigated.

These researchers evaluated the impacts of the increase of the oxygen selling price combined with a percentage decrease in the capital cost of the PEM electrolyser in order to understand what implications it might originate [11](figure 8).

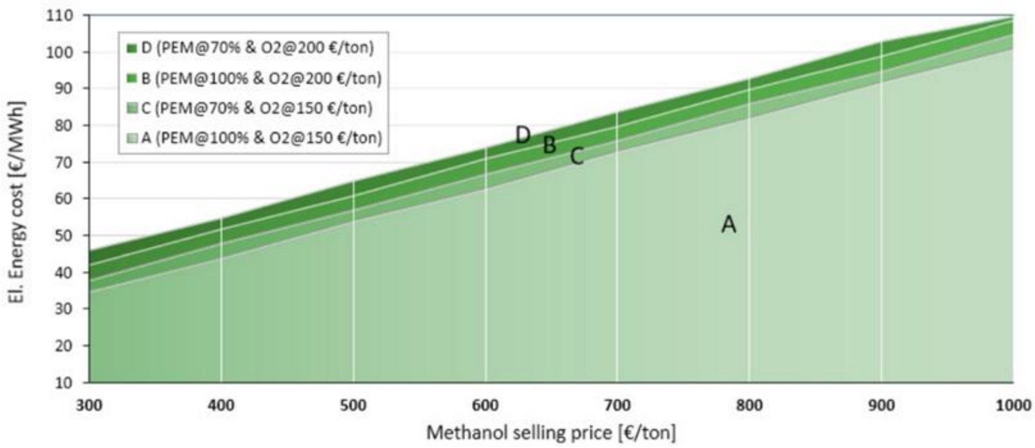


Figure 8 - Impacts of the increase of the oxygen selling price and of the decrease in the capital cost of the PEM in terms of an increase in extension of the PBP < 10 years area [11]

A major conclusion that can be taken from the previous graphic is that an increase in the oxygen price has a bigger influence than a decrease in the PEM capital cost, thus enabling a larger area extension.

Lastly, it can be assumed that oxygen and methanol selling price will directly affect the final equivalent price whereas carbon dioxide price has very little influence, which is underlined by figure 9 [15].

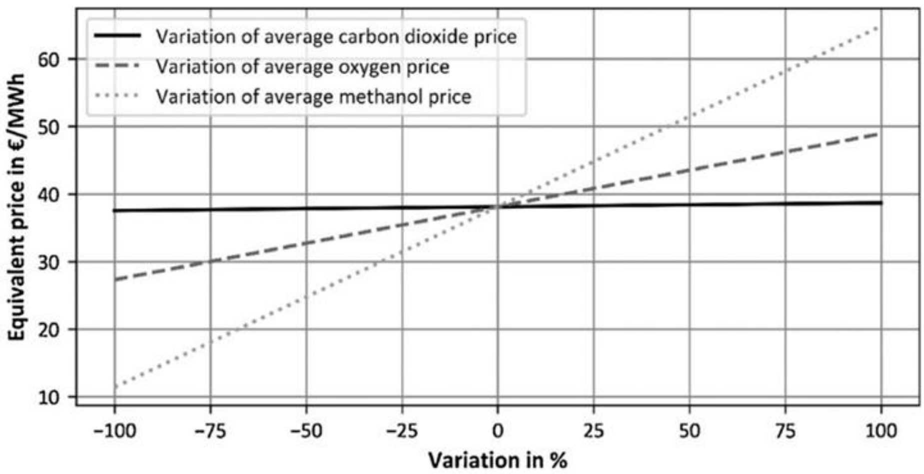


Figure 9 - Resulting equivalent price for a variation of the average prices of carbon dioxide, oxygen and methanol [15]

#### 2.2.1.2 Bio-methanol from $CO_2$ Hydrogenation

Currently the methanol production from natural gas accounts for approximately 80% of the total methanol produced worldwide [16]. In order to reduce the carbon dioxide emissions associated to such process, new technologies emerge, enabling bio-methanol production. In a recent study performed in Brazil [16], syngas obtained from biomass gasification was compared to $CO_2$ hydrogenation for large-scale application purpose. Biomass, however, present some disadvantages regarding not only its low energy content but also the fact that it requires supplementary steps related to gasification, cleaning and conditioning. It becomes inoperative for large methanol production, due to cost and ecological concerns. Therefore, bio-methanol production by $CO_2$ hydrogenation appears as the cleanest and encouraging pathway.

Due to the abundance of sugarcane in Brazil, the possibility of electrolysers efficiently arranged being powered with surplus energy provided by cogeneration units of Brazilian sugarcane mill was studied, and very promising results were reached [16].

In this process, carbon dioxide is captured from the fermentation process in ethanol production distilleries and the hydrogenation consists in three main steps: initial gas compression, followed by methanol synthesis, and lastly the synthesized methanol is purified.

With special focus in the total amount of oxygen produced from the Brazilian distilleries, the following quantities in tonne/year were registered: 1719.5 for a small distillery, 2364.4 for medium size distillery and 3009.2 for large scales distilleries [16].

The oxygen selling price was considered to vary between 187.9 and 228.8 €/tonne [16]. This means that from bio-methanol production, it could be obtained as by-product about 323094 € worth of oxygen a year, considering minimum oxygen price and a small distillery as reference. For large distilleries, and also for the case of maximum oxygen selling price, a value of 688505 €/year could be reached. In fact, oxygen re-selling is a determinant factor in the final economic assessment of any industrial process, in particular when supposedly high-cost water electrolysers are involved.

In a more realistic scenario, assuming not all by-product oxygen produced could be sold for other industrial purposes, oxygen could also be directly used in parallel processes in ethanol distilleries, such as ethylene glycol, in order to accumulate the final outcome.

Note that in Portugal, such process to obtain bio methanol might not have a big impact, since there are no ethanol production distilleries. Nevertheless, the impact of oxygen re-selling prices has shown very promising results. For this reason, further studies should focus on powering the electrolysers with wind or solar energy surplus or even biomass, in the case of reduced scale applications.

### 2.2.2. Synthetic Natural Gas

Synthetic natural gas (SNG) is a fuel gas mainly composed by methane which can be produced from fossil fuels such as lignite coal, from biofuels (called bio-SNG) or using electricity with Power-to-Gas systems. As a matter of fact, Power-to-Gas technologies will be indispensable for countries like Portugal in an energy transition scenario. One of the key arguments is the possibility to take advantage of existing network infrastructure, gradually decarbonizing the national gas network. Moreover, Power-to-Gas applications provide continuous availability and reliability in energy storage. Many projects are already being developed regarding efficient ways to inject hydrogen in the natural grid, without needing to change the grid structure.

A recent study called “Production of synthetic natural gas from industrial carbon dioxide”, published in Belgium, shows that direct injection up to 10% of hydrogen into the natural gas grid or converting it into synthetic natural gas (SNG) by methanation and subsequent injection into the gas grid are already being strongly considered [17]. In order to increase such percentage, existent grid structures should be modified, thus increasing exponentially the cost involved. In a Power-to-Gas plant, after efficient separation of the carbon dioxide from the flue gas, a methanation unit is required for further conversion of both $CO_2$ and renewable $H_2$ by a methanation reaction into SNG [17] (figure 10).

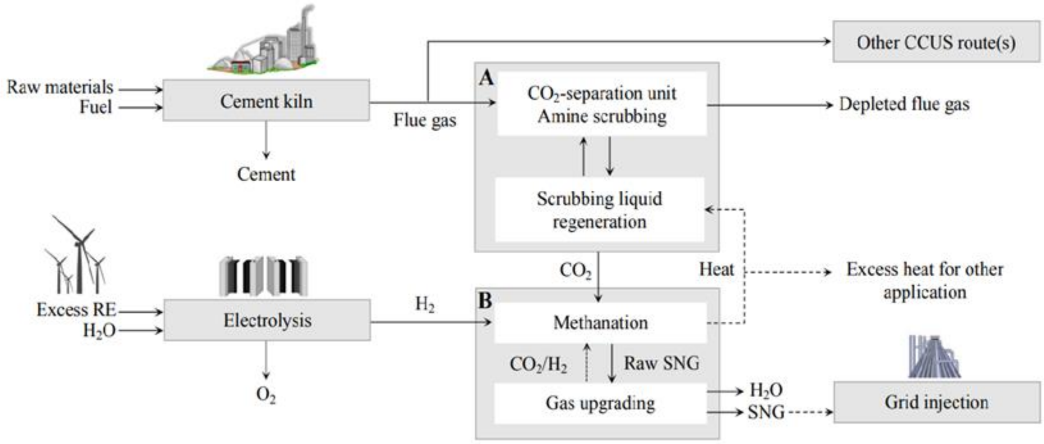


Figure 10 - Plant layout of a PtG system [17]

Analysing the electrolysis unit, the previous study considered a by-product oxygen selling price of 87.4 €/tonne [17], which is produced in high purity. Furthermore, the electricity price from renewable sources was assumed to represent about 70% of the cost of producing SNG [17]. In fact, costs related to the capital expenditures and the electrolyser efficiency only represent approximately 10% on the final SNG cost. The major conclusion obtained from R. Chauvy´s analysis was precisely the economic effect which oxygen re-selling would have in the final sensitivity analysis of the PtG plant, as shown in the diagram below [17](figure 11).

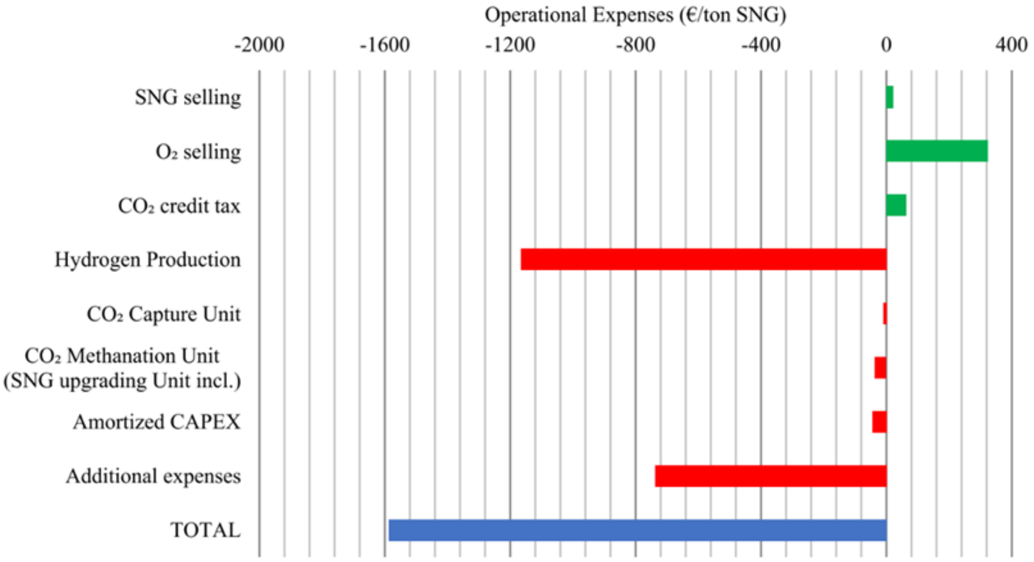


Figure 11 - Operational expenses in € per ton SNG [17]

### 2.2.3 Membrane separation technology based on ceramic membrane material vs. conventional cryogenic separation technology

Currently, in the majority of the cases, industries tend to use cryogenic air separation technology due to its high purity content (oxygen concentration ≥99%) [18]. In fact, amongst all technologies available, only water electrolysis is expected to become competitive with cryogenic air separation for large scale applications.

Conventional cryogenic air separation is not appropriate for limited onsite oxygen production, since it consists in a complex operation: initial air compression followed by air pre-treatment, the presence of a heat exchange, the cryogenic separation process itself and lastly oxygen compression. Hence, such process is only feasible for high quantities of oxygen produced, superior than 100 to 300 tonnes/day [18]. Other characteristic of cryogenic distillation is the fact that it operates at ultra-low-temperatures, where air is filtered and compressed to about -185 $°C$ [18]. Thenceforth, liquid form air is distilled and separated into all its components (nitrogen, oxygen and argon and other gases).

Each year, approximately 100 million tonnes of oxygen are produced every for a variety of industries worldwide [18]. As climate policies regulations become more restrict, renewable energy technologies are expected to increase in the near future, thus requiring considerable amounts of oxygen as feedstock. In fact, the chemical industry already claims that it will require large quantities of oxygen for **oxyfuel combustion** and **oxygen-blown gasification**, for instance. These processes are used to convert fossil fuels such as coal and methane into synthetic natural gas, which can be later refined to generate electricity or even produce transport fuels.

Nevertheless, cryogenic air separation is already becoming a very mature technology. This conventional and well-established process depends on enhanced performance components, mainly the turbine, compressor and heat exchanger in order to increase the overall efficiency.

In fact, the oxygen obtained from cryogenic distillation, which can then be used for oxyfuel combustion power plants and coal gasification, compromises the power generation efficiency about 30% below the reference value [18].

Besides cryogenic air separation, there are other existing technologies which operate at ambient temperatures, such as pressure swing adsorption (PSA), or membrane separation process, where these membranes are normally made of polymers with very specific mechanical properties.

Furthermore, an innovative air separation technology is being tested in the gas industry market, which consists on specially designed ceramic membranes that separate oxygen from air at extremely high temperatures, in opposition to conventional cryogenic air separation. According to S.S. Hashim et al., this pathway will be crucial for large scale oxygen supply applications, enabling reductions in the final capital cost and also decrease the overall energy consumption [18].

**Swing Adsorption air separation**

Swing adsorption (SA) is already used in air separation for oxygen production in many small-scale industries, which require up to 20 –100 tons of oxygen a day. Some advantages of this process are the high maturity level, the process efficiency, the adsorbents availability and also the low energy cost compared to cryogenic air separation [18]. The main systems which rely on this technology are vacuum swing adsorption (VSA), pressure swing adsorption (PSA) and temperature swing adsorption (TSA). These processes use specific absorbent materials, mainly zeolites to capture nitrogen in order to produce oxygen with purities from 90% to 95% [18]. Vacuum swing adsorption oxygen generation systems are actively used in glass fabrication, steel industry, wastewater treatment, pulp bleaching, and even in mining industries [19]. Pressure and temperature swing adsorption, however are mainly used for $CO_2$ sequestration, which is then utilized for large-scale industrial synthesis of hydrogen or in the production of ammonia.

**Mixed ionic–electronic conducting ceramic-based membranes**

As a result of the limitations and high maturity level of conventional cryogenic air separation, a new technology emerges with significant potential por large-scale applications. Contrarily to cryogenic distillation, the separation of oxygen from air is performed at extremely high temperatures, normally around 800 to 900 °C [18]. This innovative technology uses elevated density ceramic membranes, which are responsible for separating the air. As the oxygen demand increases, the gas industry is continuously investing in efficient techniques to obtain high purity oxygen, with special focus in ceramic membranes with mixed ionic–electronic conducting (MIEC) attributes. What is so attractive regarding these ceramic membranes is the fact that they do not depend on electrodes nor do they need an external circuit to transport the ions [18]. Currently, some industrial processes such as gasification and oxyfuel combustion systems present considerable efficiency losses, in particular during the carbon dioxide capture and storage phase. Such effect is directly related to the immense energy demand for oxygen production, which cryogenic distillation requires. For this reason, ceramic membrane separation is expected to become the most dominant technology regarding air separation, replacing cryogenic air separation in the energy transition future. Nevertheless, there are still several concerns that need to be properly studied in order to become a viable technology in the market. More specifically, the ceramic material is still a big obstacle, since it has to be able to sustain the high temperature which MIEC membrane air separation require. In fact, density and stability are some of the many properties which present extreme importance. Below is presented a model representation of the oxygen transport in dense MIEC ceramic membrane [18](figure 12).

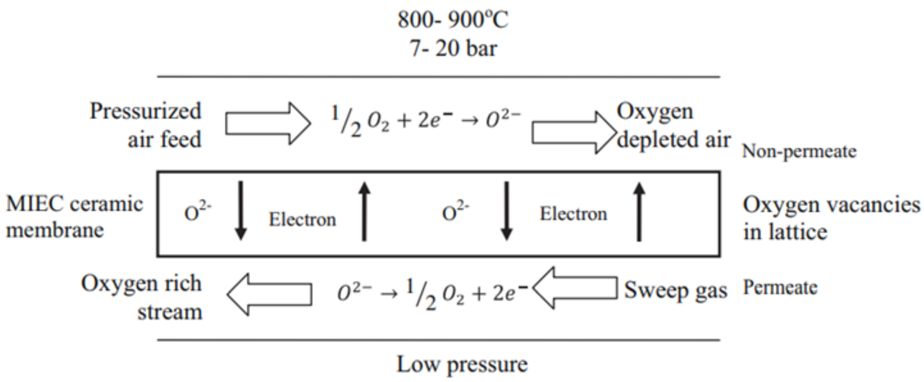


Figure 12 - Schematic representation of the oxygen transport in dense MIEC ceramic membrane[18]

As it can be seen in figure 12, oxygen passes through from the elevated pressure side to the low oxygen pressure side, without changing the overall neutrality of the process, due to the outweigh of the electrons.

In such manner, ceramic membranes, along with water electrolysis are expected to overcome cryogenic technology for sizable proportions of high purity oxygen supply. Moreover, studies have shown that MIEC ceramic membranes are likely to reduce oxygen energy costs by more than 35% when compared to the cryogenic separation technology [18]. Nevertheless, high temperature air separation technique is still underdeveloped in the industry market, which makes some gas suppliers slightly reluctant towards such process. Table 2 presents a comparison between the current air separation techniques available in the market, comprising their maturity, by-product capability and oxygen purity level (in vol.%).

Table 2 - Comparison between air separation techniques for oxygen production

| **Process** | **Maturity** | **By-product capability** | **Purity level (in vol.%)** |
|---|---|---|---|
| Cryogenic | Mature | Excellent | 99+ |
| Adsorption | Semi-mature | Poor | 95 |
| Polymeric membrane | Semi-mature | Poor | approximately 40 |
| Chemical | Developing | Poor | 99+ |
| Ceramic Membrane | Developing | Poor | 99+ |
| Water electrolysis | Developing | Excellent | 99+ |

#### 2.2.3.1. Oxyfuel combustion

**Power to Gas - Oxycombustion hybridization**

A very promising application of by-produced oxygen is the hybridization of Power to Gas system, with oxyfuel combustion. Such process has particular interest, since instead of using air, the process comburent consists in a mixture of recycled flue gas from the powerplant and pure oxygen [20]. The combustion products are mainly $CO_2$ and $H_2O$ and the flue gas has a high carbon dioxide concentration, after the steam condensation occurs. Currently, such process is still under efficient, due to several reasons. In fact, a recent study regarding future hydrogen applications and the use of $CO_2$ as an energy storage medium [20], reached a very interesting conclusion. The energy penalty related to carbon capture and sequestration was estimated to be around 190 kWh per each oxygen ton [20]. This value is a direct consequence of the air separation technique used to obtain oxygen, which normally is conventional cryogenic method. Another study reported that the process of cryogenic separation consumes about 15% of the global electrical output of the oxyfuel powerplant. In fact, the energy penalty associated is assumed to vary from 220 kWh/t$O_2$ to 245 kWh/t$O_2$[18]. As renewable energy sources become competitive, water electrolysis is foreseen as a very promising technique. Subsequently, pure oxygen would be obtained and the final energy cost would be reduced, since it highly depends on the air separation process.

Furthermore, hydrogen and oxygen from the electrolysis could be stored in order to tackle renewable energy intermittency. The hybridization of power to gas plants would increase the overall efficiency of the plant, as well as reducing fossil fuel emissions. European countries with high solar and wind energy resources, as it is the case of Portugal, would truly benefit from this system. During periods of renewable energy surplus, energy would be stored as hydrogen and oxygen for further applications. Under circumstances where wind of solar energy would not be enough to power the electrolyser, the combined cycle powerplant could still produce electricity, by using the stored oxygen for the oxyfuel combustion process. Meanwhile, the methanation process uses renewable hydrogen and $CO_2$ from the power plant flue gas. The exothermal heat from methanation can further be reused as low-pressure steam in the steam cycle of this cogeneration plant, increasing the overall efficiency.

Finally, synthetic natural gas is obtained, which can be injected in the national grid, or used to power the gas engines of the combined cycle powerplant. Hence, oxyfuel combustion hybridization would increase the overall efficiency and become a carbon-neutral process, meeting the energy transition political demands.

**Ceramic Membrane for Oxyfuel combustion**

As previously explained, Oxyfuel combustion, also called oxy-combustion uses an oxygen stream instead of air for combustion. The exhaust combustion flue gas has a high concentration of carbon dioxide (above 90% [18]), whereas avoiding nitrogen inside the system.

In order to reduce the energy penalty related to the cryogenic air separation unit, a ceramic membrane with ionic electronic conduction attributes can be implemented in an oxy-combustion powerplant. In this technology, air is compressed up to 10 bars [18].

As previously shown in figure 12, the air separation occurs at temperatures above 800 °C and oxygen penetrates from the elevated pressure side to the low oxygen pressure side. In order to obtain the necessary heat to reach such elevated temperatures, researchers are currently studying the combination of air compression, reuse of the flue gas and also the boiler heat exchanger efficiency.  One particular advantage of the ceramic membrane module is that it can be implemented at the leading end of the oxyfuel combustion plant. As a consequence, captured $CO_2$ from the combustion process enables a constant reduction in the oxygen pressure across the membrane. Then, oxygen penetrates through the ceramic membrane, upgrading the recycled carbon dioxide in about 20% (v/v) [18]. Ultimately, the oxygen enriched $CO_2$ stream is heated in the boiler, and the steam turbine generates electricity. This process is summarized in the figure below (figure 13 [18]).

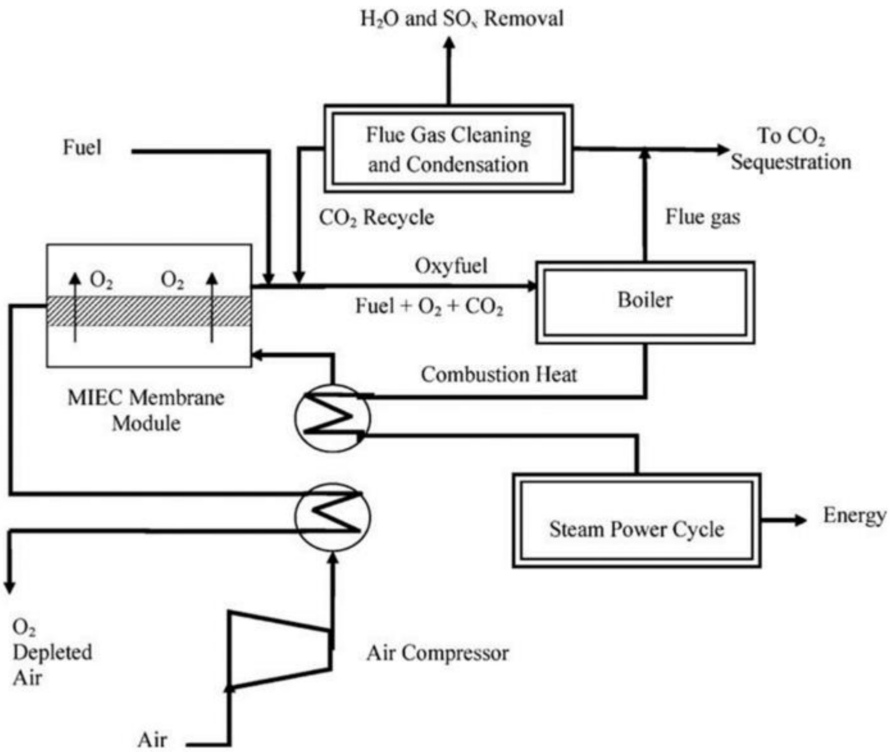


Figure 13 - Oxyfuel power plant with a MIEC membrane module [18]

### 2.2.3.2. Coal Gasification

Coal Gasification is also a very interesting application which consumes oxygen. A gasification system is an endothermic process which consists in obtaining synthesis gas from feedstock rich in carbon. Such syngas is mainly composed by hydrogen and carbon monoxide, and is further used as fuel amongst other chemical applications previously discussed. Different feedstocks can be used in gasification processes, namely coal, petroleum coke or even biomass and organic waste. Nevertheless, coal has the highest syngas capacity for commercial applications in the world, followed by petroleum [10]. Coal gasification for industrial purposes enables high plant efficiencies while emitting extremely low quantities of sulphur and nitrogen oxide into the atmosphere [18]. Biomass and municipal solid waste are the least used for large-scale applications due to its low energy content.

Hence, gasification can be directly applied in cogeneration powerplants, more specifically, in integrated gasification combined cycle (IGCC) systems. The syngas obtained operates as a fuel to generate electricity from the powerplant, since it can be reused to drive the steam turbine. Moreover, gasification processes required external heat to produce syngas. In fact, a partial combustion reaction is used in most cases, in particular with an oxygen blown gasifier. Oxygen used for gasification requires 95% [21] purity level, which is currently obtained by conventional cryogenic air separation. Even though oxygen has favourable heating value properties, the energy consumed in the air separation unit should not be neglected, which corresponds to 10% of the overall power produced from the IGCC [21]. In order to reduce the capital costs involved in the oxygen blown gasification process, the prospect of by-product oxygen must be addressed.

As in the case of oxyfuel combustion powerplants, gasification processes would also benefit from an enhanced air separator unit (ASU), more specifically the replacement of the conventional cryogenic technology for ceramic membranes. Such method is expected to increase the efficiency of IGCC power plants, while reducing the energy consumption of the ASU. The figure below illustrates the incorporation of the ceramic membrane in a coal IGCC plant [18](figure 14).

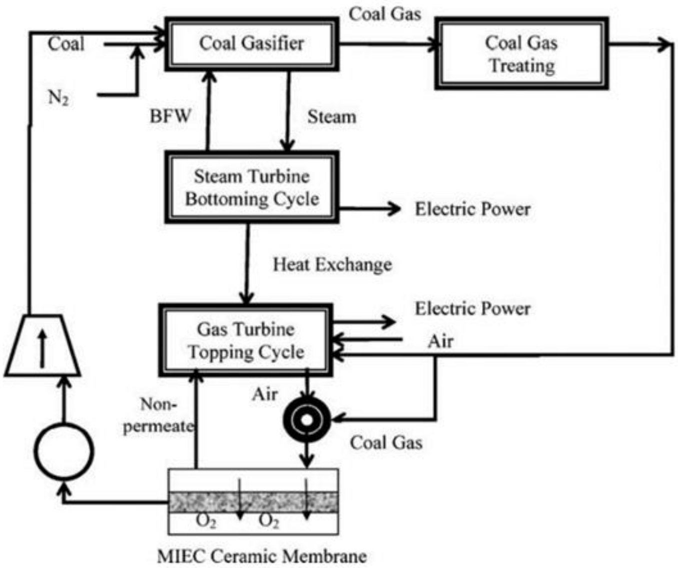


Figure 14 - Coal gasification IGCC power plant with a MIEC Ceramic Membrane [18]

It is noteworthy to analyse the differences between MIEC incorporation in gasification powerplants from oxyfuel combustion systems. In the oxy-fired powerplant, the ceramic materials should not be affected by the presence of carbon dioxide in the permeate side. On the other hand, the ceramic membrane used for coal gasification processes must be invulnerable to the steam from the turbine, as it can be seen from the above power plant layout [18].

In conclusion, stress and fatigue properties of the chosen ceramic for the membrane have to be meticulously tested prior to its application. Nevertheless, MIEC membranes are a very auspicious technology for coal gasification systems in the future, in particular for tonnage supply of oxygen from air separation.

#### 2.2.3.3. Progress in zero emission combustion

As already discussed, by-product oxygen has many advantages, such as compensating for renewable energy sources intermittency, increasing powerplants overall efficiencies and reducing capital costs and energy consumption. Furthermore, the use of by-product oxygen is a very promising way to accomplish zero emission combustion target.

In fact, a research project was performed called OXYCOAL-AC [22], which main goal was to develop an integrated power plant process, combining a shattered fuel in a mixture of recirculated flue gas (RFG) with oxygen, which should be obtained using a ceramic membrane air separation technology. This project relies on oxy-combustion processes, where coal is burnt in a mixture of oxygen and recycled flue gas.

Nowadays, conventional coal combustion powerplants are responsible for great amounts of $CO_2$ emissions into the atmosphere. Hence, in order to meet climate change targets, existing powerplants should be adapted into zero emission systems, without affecting the electricity generated nor its efficiency. Despite the current $CO_2$ Capture and Storage (CCS) technology being already implemented amongst several coal powerplants, there are still some disadvantages. In particular, cost related to the considerable mass exchangers required is a big obstacle. Safety regarding appropriate carbon dioxide storage is also a big concern.

In this way, oxyfuel technology offers the possibility to increase the carbon dioxide presence in the flue gas. The RFG is composed by water vapour and $CO_2$ with up to 90% concentration [15]. Further cleaning and compression of carbon dioxide was assumed to consume 130 kWh/tonne of $CO_2$ [22]. In terms of the air separation for oxygen production, cryogenic distillation requires about 240 kWh per ton of $O_2$. Studies show that the above processes cause the total efficiency of the power plant to fall by 8 to 10% [22].

If an ionic ceramic membrane was used instead, the efficiency deficit would be smaller. Besides, cost reduction can be attained, by improving the oxyfuel combustion operation at low oxygen concentrations. The current energy demand for ceramic membrane oxygen production is 100 kWh/tonne of $O_2$, which is less than half compared to cryogenic air separation. However, such technology is still in developing process, meaning in the future researchers predict that it could consume only around 30 kWh/tonne of oxygen [22].

In conclusion, MIEC membranes are already replacing cryogenic air separation technology. Developments still have to be made regarding the membrane´s resistance to $CO_2$ and SOx, maintaining permeability to oxygen. Coal oxyfuel combustion presents an efficient carbon neutral rising solution, with great advantages for commercial purpose, particularly for European countries with increasing climate regulatory regimes.

### 2.2.4 Glass Melting Furnaces

Oxygen-blown combustion can be used in glass melting industries in order to reduce the energy consumption of the process. Moreover, when compared to air-blown combustion, oxygen reduces drastically both $CO_2$ and $NO_x$ emissions into the atmosphere.

In a glass melt furnace, chemical reactions occur at extremely elevated temperatures, from 1400 to 1500 °C [23]. The melting process requires external heat to initiate, which is normally provided by oil or natural gas combustion. However, many industrial large-scale glass furnaces integrate regenerative heat-recovery systems, since energy losses typically account for 40% of total heat input [10]. Such regenerative devices present two refractory chambers in order to absorb heat from the flue gas and preheat the combustion air.

With the purpose of reducing these losses, oxyfuel glass furnaces are assumed to be the best alternative. In fact, a recent study estimated that an oxyfuel furnace consumed 3.4 to 3.6 MJ/kg of glass, which accounts for both preheating the recycled glass and also the energy demand for oxygen production [23]. It is important to note that these values were obtained considering a 50% glass recycling in the glass batch. If 100% cullet was considered, the energy consumption would drop to 2.5 MJ/kg [23].

Comparing these results with conventional air-blown combustion melting process, the energy consumption was around 11 MJ/kg of glass [10], which is significant larger. It is presented below the contrast between air and oxygen-blown technologies, in terms of energy consumption and fossil fuel emissions [10](figure 15).

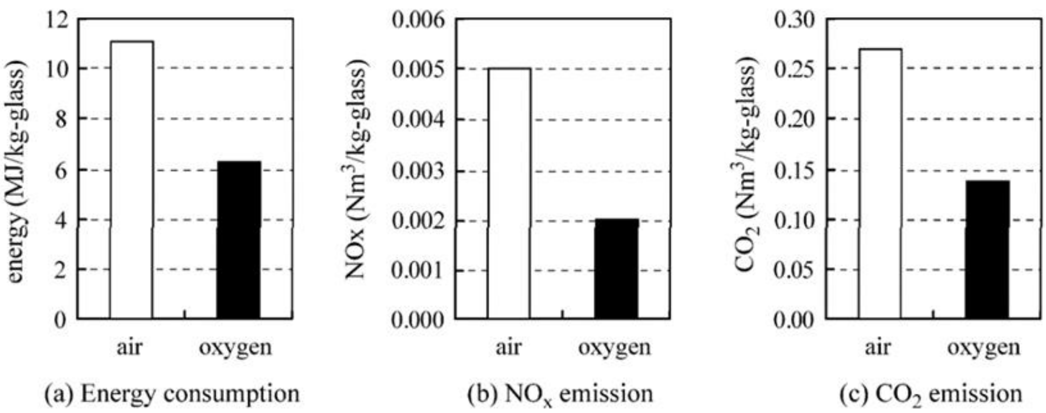


Figure 15 - Comparison between air-blown combustion and oxygen-blown combustion in glass melting[10]

Analysing the energy consumption, the melting process efficiency can be improved by 40% with oxygen-blown combustion. Moreover, the oxygen demand for the oxygen combustion furnace is about 400 kg $O_2$/tonne of glass. Also, the energy consumption per unit of oxygen decreases 12 MJ/kg $O_2$ [10].

With regard to fuel consumption for glass melting, significant improvements are obtained. Neglecting the energy required for oxygen production, the oxygen fired scenario enables an achievement of 16.7% less natural gas than the air combustion case. If both oxygen and the fuel used are pre-heated in separated heat exchangers, further improvements could be gained in the overall heat recovery system. In fact, incorporating these heat exchangers allows natural gas consumption to decrease up to 23.8% when compared to reference case glass melting process [23].

Presently, conventional cryogenic distillation and pressure/vacuum swing adsorption are the most used techniques for industrial applications, due to the ability to obtain high purity oxygen (larger than 99%). Nevertheless, recent studies contemplate the ceramic membrane alternative as a better solution for oxyfuel glass melting processes [23]. Such option can even generate electrical power to the system, besides providing oxygen to the furnace, with the purity level required.

The main adversity of ceramic membranes is the high temperature into which the fuel must be heated, thus increasing energy consumption. Antonio Giuffrida et al. estimated that the use of such membranes requires an amount of 291.6 kg/h of fuel, which is higher than the fuel demand for the regenerative heat recovery system case (235.7 kg/h of fuel). However, both scenarios suggest a significant improvement in comparison to the reference melting process, which has a fuel demand around 309.3 kg/h [23]. Further research should be done, with the ultimate goal of incorporating both ceramic membranes and heat recovery systems in the same melting process.

Despite these advantages, oxygen combustion still present economic barriers for large scale industries when compared to the conventional air combustion. However, as regulatory measures increase both fossil fuels price and carbon taxes, oxygen combustion will have a bigger penetration in the glass melting market, especially if the oxygen source can be from the water electrolysis.

### 2.2.5 Metal fabrication

Oxygen is widely used in the iron and steel fabrication, in particular for both blast and electrical furnaces.

One variation of oxyfuel combustion processes which is adopted for iron making is Oxygen Blast Furnace (OBF). As a matter of fact, oxygen increases the efficiency of $CO_2$ capture in the process, since the blast furnace gas has higher carbon dioxide content. Thereafter, the remaining furnace gas, mainly composed by carbon monoxide, is recycled and injected in the blast furnace. Ultimately, oxygen contributes for reducing the carbon consumption of steel production, as well as to minimize the coal/coke fuel consumption in the process.

Furthermore, oxy-combustion processes are constantly being investigated in order to reduce fossil fuel emissions, as well as to improve the economic feasibility of steel production. Oxygen blast furnace processes are one of the most dominant industrial oxygen consumers in the market. Since large quantities of oxygen are required for iron making, most industries produce such gas on site. Thereby, in order to reduce the costs correlated to $CO_2$ capture, the air separation unit (ASU) represents a major concern.

Gas companies such Air Liquide have been continuously improving the ASU efficiency, incorporating heat integration systems. In 2015, cryogenic air separation units consumed 140 kWh/ton of $O_2$, whereas in 2020 a value of 120 kWh/t was obtained [24].

With the aim of reducing the energy consumption of oxy-combustion plants, Air Liquide developed a system based on energy storage, which consists in running the ASU and the boiler in different phases. Thereby, it would be possible to store and deliver oxygen in liquid form, according electricity demand [24](figure 16).

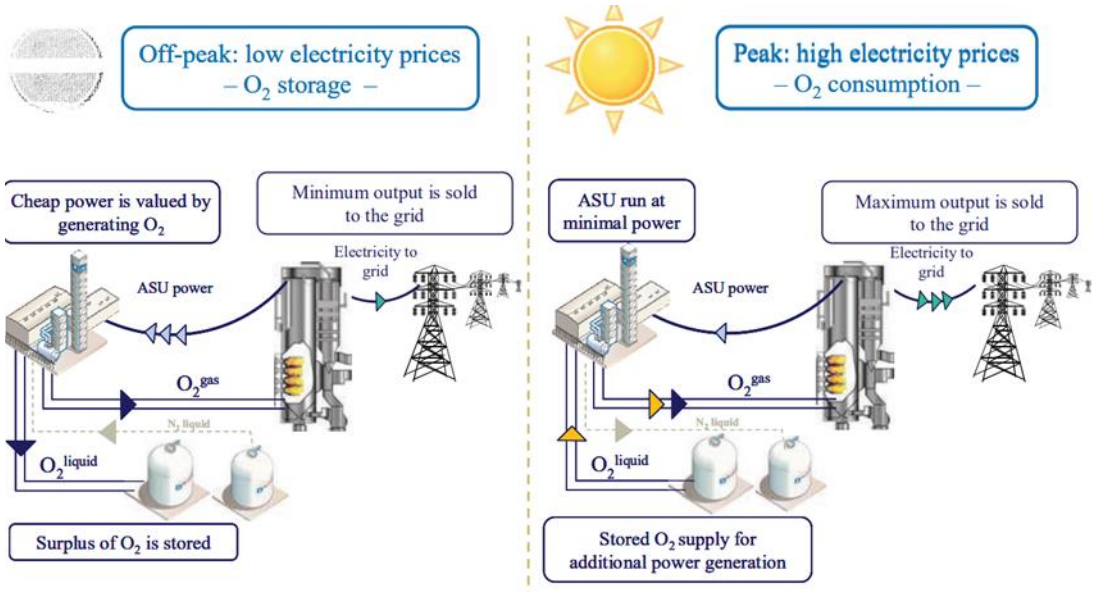


Figure 16 - Energy storage system [24]

A reference 575 MW oxyfuel power plant with 85% capacity factor and an oxygen consumption of 11 000 tonnes per day was considered by Air Liquide to assess the benefits of such energy storage system. Furthermore, the power plant was assumed to be in operation 100% during the day (corresponding to 16h at 575MW) and 50% during the night (equivalent to 8h at 285 MW). While the boiler was operating at maximum production (100%), the air separator unit net power decreased by 33%, from 88 MW to 59 MW during a 12h operation period, while the boiler net power increased by 5%, reaching a value of 604 MW during the same period time [24]. Note that a common coal oxy-combustion plant needs between 5 000 and 15 000 tonnes/day of $O_2$ (approximately 20 tonnes per day of $O_2$ / MW) [25].

The results obtained were an increase of 5 to 10% in the net power output available at peak time, a contraction of 15% in the ASU cost and finally a reduction of 10% in the oxygen production cost [24].

Nevertheless, cryogenic distillation has reached its maturity level and still contributes for significant carbon emissions. In order to reach climate targets other alternatives should be implemented. In particular, by-product oxygen from water electrolysis is a promising option as green hydrogen demand is drastically increasing. The main obstacle is, of course, the high energy consumption of the electrolyser, which needs to be powered by renewable energy surplus.

Lawrence Hooey et al. [26] performed a thorough comparative between air blast furnace and oxygen blast furnace, considering a 4 million tonnes hot-rolled coil annual production as reference case. The differences between both processes are noticeable. In fact, in terms of electricity demand, OBF requires 573 kWh/tonne of hot-rolled oil whereas air blast furnace consumed 400 kWh per tonne (about 30% less). Naturally, oxygen blast furnace has considerable larger oxygen demand, around 435 kg per tonne of hot-rolled coil produced. Traditional blast furnace only requires 162 kg of oxygen per tonne. It is also interesting to analyse the fuel demand. OBF requires 311 kg of coke per tonne produced, which represents a reduction of 24% compared to the reference process.

Moreover, in order to determine the carbon reduction associated to the oxygen blast furnace, the overall operating system was analysed. Considering a constant gas recycle rate of 82%, an estimated amount of 817 kg of $CO_2$ per tonne of hot metal was captured and further compressed [26]. A schematic oxygen blast furnace is presented below, where it can be seen the high content of CO in the recycled process gas (around 67%) after $CO_2$ sequestration[26] (figure 17).

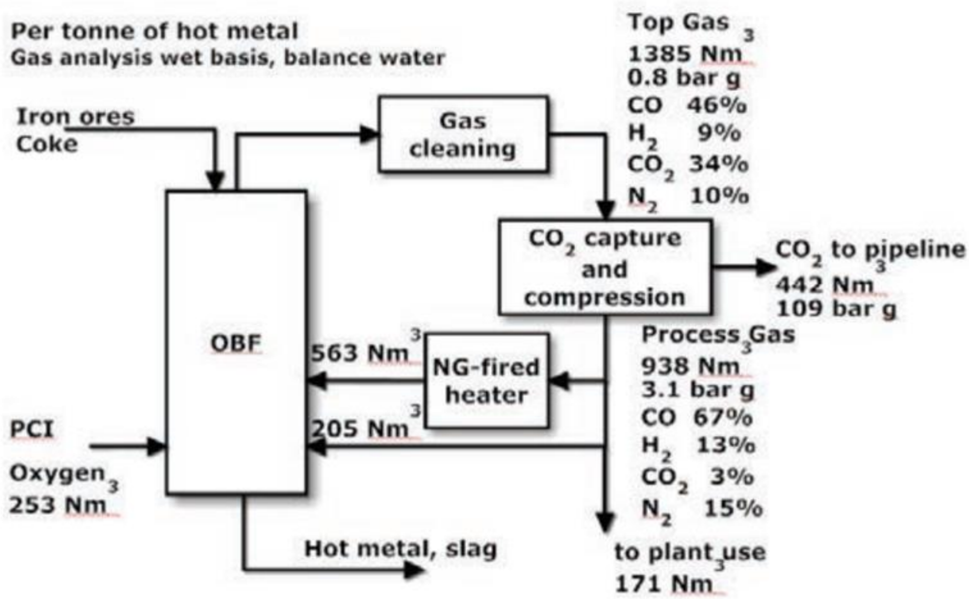


Figure 17 - Oxygen blast furnace system [26]

In fact, the main European steel production companies in the market, which integrate the ULCOS (Ultra Low $CO_2$ Steel Making) society, are already promoting oxygen enriched blast furnaces with the aim of reducing by 50% the quantity carbon dioxide emitted [24]. Air Liquide has been very attentive regarding carbon emissions as well as to increase the global efficiency of the furnace. In fact, a technology called "*Cryocap Steel*" was proposed. This solution consists in the incorporation of both a Pressure Swing Adsorption unit and a Cryogenic purification unit in the overall system. As it can be seen in figure 18 [24], the PSA is used in a cyclical process to compress the blast furnace gas prior to $CO_2$ separation. Subsequently, the remaining carbon dioxide is further purified in the cryogenic unit, which enables almost complete carbon monoxide recovery.

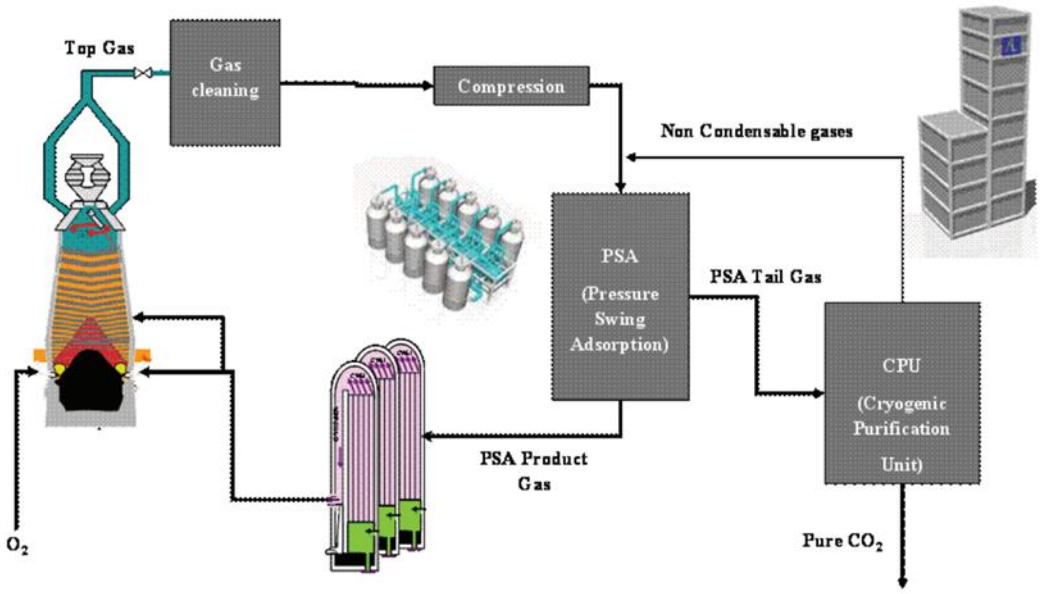


Figure 18 - Enhanced Oxygen blast furnace system[24]

Besides increasing the steel making process efficiency, the presence of oxygen also improves the calorific value of the blast furnace top gas. Whether coal or coke is being used as fuel, after top gas cleaning, a promising application might be its integration in a combined gasification cycle process. According to Y. Jianwei et al. [27], per each ton of hot metal produced, twice the coal gas is obtained. Furthermore, in contrast with air gasification, which delivers a coal calorific value between 4470 and 6710 kJ/Nm$^3$, oxygen provides higher energy content of up to 11180 kJ/Nm$^3$ [27].

In fact, since conventional coal powerplants are being shut down due to fossil fuels emissions, combined cycle plants have gained great relevance. Thus, the oxygen blast furnace with a cogeneration power plant implements both extensive steel making and electricity generation [27]. Moreover, the combined cycle integration aims to increase the operation efficiency, rather than solely reducing fuel consumption. Oxygen blast furnaces promote an increase in the blast gas flowrate, thus improving the steel production operation. In fact, as oxygen acts as an oxidizer agent, the resultant slag from the iron smelting is minimum.

Such process also enables a reduction in the steel production cost, when compared to the conventional blast furnace. Oxygen improves the overall combustion reaction, which increases coal pulverization. Thus, a combined cycle power plant promotes an increase in the metal production, while reducing coke emissions. Conclusively, oxygen blasting with a cogeneration system is assumed to be a sustainable and competitive option to replace existing coal powerplants.

Another oxygen application for iron making with great commercial relevance is electric arc furnaces. Compared to blast furnaces, this alternative for metal production has considerably less oxygen demand. For this reason, there is no need to produce such gas on site. In fact, electric arc furnaces economic evaluation has greater dependability on both the oxygen market value as well as the operation heat efficiency. A study performed in Japan concluded that the current electricity consumption for electric arc furnace steel production is about 150 kWh per tonne of steel, with an oxygen consumption of 60 kg /tonne of steel [10].

In conclusion, a comparison between the oxygen demand for blast furnaces and electric arc furnaces can be made. As a matter of fact, oxygen blasting requires more than 7 times the amount of oxygen than the electric arc technology. For the case of traditional blast furnace, the difference is smaller, with an oxygen demand for conventional air blast furnace 3 times larger than electric furnace. Either way, the iron making process is a very important oxygen consumer. As many other industries described throughout this work, continuous efficiency improvements are essential in order to accomplish the climate targets imposed by European governments, with special focus on reducing fossil fuels emission of any kind.

### 2.2.6 Paper pulp bleaching

Oxygen is widely used as a reagent to improve pulp bleaching. In fact, due to the high oxygen demand, the paper production industry tend to adopt on site production. The main oxygen application is in pulp delignification, which consists in extracting the darkened lignin from the pulp after the cooking process. For this primary step, the oxygen demand varies between 20 and 30 kg of $O_2$/tonne of pulp [28].

Subsequently, oxygen bleaching is used, in order to remove the remaining lignin and existing resins. Bleaching process consumes around 10 to 15 kg of $O_2$ per tonne [28] and is used as an additional step rather than an alternative for delignification process. Oxygen is acknowledged as the most efficient bleaching agent. Nevertheless, costs related to its pressurization should not be neglected, with required pressure values between 390 and 780 kPa [29]. Moreover, pulp bleaching processes can be subdivided in elemental chlorine free (ECF) and totally chlorine free (TCF). In fact, TCF combines more the one reagent, namely oxygen, ozone, hydrogen peroxide, peroxyacid and peroxysalts [29] to improve the quality of the bleaching process. Peroxide at high pressures increases the paper brightness while it can further be used to decrease chlorine dioxide consumption, for the case of ECF.

Oxygen can also improve alkaline extraction. This process is used as an additional step, after the bleaching stage with the purpose of increasing lignin dissolution as well as to improve brightness. Despite the fact that the primary chemical used for this stage is sodium hydroxide (NaOH), oxygen and hydrogen peroxide at high temperatures can be combined to enhance the process. For this stage, typical $O_2$ consumption is around 5 kg/tonne [28].

Another interesting application of oxygen is in lime kilns processes [30]. Such operation is based on calcination process, given by the following reaction:

$$CaCO_3 + heat \rightarrow CaO + CO_2 \quad (2)$$

In order to increase the production rate of lime kiln operation, oxygen can be added, improving the combustion efficiency. Furthermore, oxygen can also reduce fuel consumption, thus decreasing carbon dioxide emissions.

Lastly, white liquor oxidation is also an important oxygen consumer. White liquor can be used to extract lignin from cellulose. It operates similar to an alkaline solution, after going through and oxidization process. Such process represents an alternative for pulp delignification, meaning it can be used as a primary step for pulp production. In fact, oxygen is used to increase the oxidation reaction of white liquor, which is mainly composed by sodium hydroxide and sodium sulphide. Note that for the sodium sulphide case, oxidation is incomplete, originating sodium thiosulfate.

In conclusion, oxygen demand for white liquor oxidation depends greatly on whether oxygen is used to enhance air combustion or as the main oxidizing agent. For economic reasons, in most cases scenario oxygen is used as an additive, with a small consumption of 5 to 10 kg $O_2$/tonne [28].

### 2.2.7 Wastewater management

Wastewater treatment is an essential application in order to comply with the sanitary conditions imposed by environmental regulators. In fact, the increasing quantities of pollutants and contaminants in treatment plants represents a big concern. The major responsible for such contamination are large scale industry applications, mainly from pulp, textiles, surface treatment plants and the food industry [31]. In fact, these industries activities are highly regulated by environmental legislation in order to assure that the minimum treatment standards are satisfied. Furthermore, the ability of further processing such pollutants and recycling them depends greatly in their respective toxicity levels as well as the biodegradable capacity.

Major pollutant industries, such as the case of agro-food, manage their wastewater treatment plants on-site. Some benefits of such decision are to satisfy regulatory requirements as well as to avoid being taxed due to effluents pollution. Large-scale on-site plants also facilitate water recycling after treatment, thus increasing efficiency and reducing capital costs [32].

In order to decontaminate water, several steps may be required, regarding the amount of chemicals and heavy pollutants in the wastewater plant. The initial step is the pre-treatment stage, mainly used to remove the solid sludge from wastewater. Despite oxygen´s low solubility in water, its use has tremendous advantages regarding oxidation reactions and also for pH adjustment, in combination with carbon dioxide. Thereafter, the purification process may undergo a secondary treatment, which can be separated into anaerobic digestion and aerobic treatment [32].

For the case of aerobic treatments, oxygen demand relies on innumerable factors, from the type of pollutant to be removed to even seasonal fluctuations in temperature [33]. In fact, when temperature increases, aerobic bacteria also tend to rise, thus requiring more oxygen to dissolve organic matter. In extreme cases, when these bacteria consume more oxygen than the amount being supplied, it may originate anoxic zones with intense odours.

The food sector, for instance, releases lighter waste pollutants than the chemical industry. Hence, different pathways should be used for each case. In fact, food industry, due to its large quantities of biodegradable content, uses oxygen activated sludge processes for water treatment. This economical technique depends on dissolved oxygen to extract wastewater effluent pollutants. Moreover, the activated sludge process produces cellular biomass through oxidation, which can later be used for biofuel production [32]. Nevertheless, additional costly processes would be required such as filtration, coagulation or reverse osmosis [34].

When compared to air-based systems, oxygen represents a much more compelling option, since it increases organic biodegradation rate. An aerobic system uniquely based on oxygen will also be able to remove larger quantities of water contaminants, thus reducing both Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD) parameters [31].

A study performed by the gas company Linde concluded that 2 mg/l of dissolved oxygen are enough to assure appropriate water treatment [32]. Furthermore, in order to validate such result, a chemical industry in Korea was closely analysed. In order to increase their production capacity, such industry opted to add dissolved oxygen in the secondary aerobic treatment stage. In fact, by adopting Linde´s solution, astonishing developments were obtained. For the aeration system, a reduction of 40% in the energy demand was recognized. As for the water quality, which was evaluated through COD criteria, up to 70% of toxic waste was eliminated [32].

In utmost pollution cases, a tertiary stage might be necessary. The most used solution for wastewater treatments is based on the Fenton´s oxidation process, due to the fact that organic decomposition can be achieved with low energy consumption [35]. Such process is based on the oxidation reaction of hydrogen peroxide ($H_2O_2$) with ferrous iron as a catalyst, and is given as the following.

$$Fe^{2+} + H_2O_2 \rightarrow OH\cdot + Fe^{3+} + OH^- \quad (3)$$

$$Fe^{3+} + H_2O_2 \rightarrow HO_2\cdot + Fe^{2+} + H^+ \quad (4)$$

In equation (3), hydroxyl radicals are formed, whereas equation (4) originate hydroperoxyl radicals. However, both radicals are further processed in order to enhance water treatment performance.

Nevertheless, some obstacles have been identified associated with Fenton´s reagent, such as the time demand, pH adjustment requirement and sludge production just to name a few [35]. For this reason, by adding dissolved oxygen in the secondary stage, the need for further processes such as the one described is reduced.

Besides conventional oxygen enhanced sludge treatments, there are also other secondary processes of particular interest. Advanced Oxidation Process (AOP) consists in the combination of ozone with hydrogen peroxide ($H_2O_2$) or UV light, and can be used for odour control [32]. For heavy waste removal from chemical industries, Supercritical Water Oxidation (SCWO) is also a viable option. For this process, temperature should be higher than 600 °C and the pressure around 250 bars [32]. Highly toxic chemical components such as polychlorinated biphenyls, which can also be found in fat tissues of animals, fish in particular, are efficiently eliminated by this severe treatment alternative. Furthermore, the energy released from the oxidation reactions can be recycled, increasing the efficiency of the treatment plant [32].

Overall, not only does oxygen avoid regulatory taxes for over pollution violations, but it can also increase the overall efficiency of wastewater treatment. Oxygen demand may vary regarding the process stage as well as the production capacity of the treatment plant. Nevertheless, an oxygen average consumption of 50 kg $O_2$/tonne is a value widely accepted regarding activated sludge processes, particularly used for processing wastewater from the pulp and paper industry [28].

### 2.2.8 Oxygen in red meat packaging

Another interesting application of oxygen is in food modified atmosphere packaging, in particular for red meat, which is more prone to bacterial growth and red colouring oxidation.

In fact, an appropriate packaging is essential not only to protect meat from bacteria but also to extend its respective shelf-life period. According to the gas company Linde, a concentration of 60 to 80% of oxygen can extend red meat expiration date from 2 or 4 days up to 8 days if conserved at a temperature around 4 °C[36]. Furthermore, apart from preserving red meat´s colour and eliminating bacteria, other applications of such gas include decent breathing rate of packaged fresh products and even to improve alcoholic drinks fermentation, mainly wine and beer [37].

Table 3 shows the gas mixture proportions which certain meat products should be packaged, as well as the shelf-life improvement when using modified atmosphere packaging (MAP) (table 3, [36]).

Table 3 - Suggested gas mixtures for meat packaging [36]

| Product | Gas mixture | Gas volume / Product volume | Typical shelf-life | |Storage temp. |
|---|---|---|---|---|---|
| | | | Air | MAP | |
| Raw red meat | 60–80% $O_2$ + 20–40% $CO_2$ | 100–200 ml / 100 g meat | 2–4 days | 5–8 days | 2–3 °C |
| Minced meat | 80–100% $O_2$ + 0–20% $CO_2$ | 100–200 ml / 100 g meat | <24 h | 3–4 days | 2–3 °C |
| Raw light poultry | 40–100% $CO_2$ + 0–60% $N_2$ | 100–200 ml / 100 g meat | 4–7 days | 16–21 days | 2–3 °C |
| Raw dark poultry | 70% $O_2$ + 30% $CO_2$ | 100–200 ml / 100 g meat | 3–5 days | 7–14 days | 2–3 °C |
| Sausages | 20–30% $CO_2$ + 70–80% $N_2$ | 50–100 ml / 100 g prod. | 2–4 days | 2–5 weeks | 4–6 °C |
| Sliced cooked meat | 30% $CO_2$ + 70% $N_2$ | 50–100 ml / 100 g prod. | 2–4 days | 2–5 weeks | 4–6 °C |

As it can be seen from the table above, carbon dioxide also plays a key role for some meat derivatives, namely poultry. In fact, $CO_2$ likewise has a constraining effect on aerobic bacteria growth, by reducing the pH value of meat. It is noteworthy to analyse the raw light poultry case, where up until 100% of $CO_2$ can be used for packaging, thus recording the biggest growth in shelf-life. The main difference between packing red meat and chicken, for instance, is that poultry does not suffer surface discoloration. In fact, its typical low shelf-life period is mostly related with the rapidly increase of bacteria.

In sum, oxygen is widely used for food modified atmosphere packaging. Its demand is of course significantly narrow when compared to the industry applications previously discussed in this study, such as glass and metal furnaces, as well as pulp bleaching. Nevertheless, its consumption should not be neglected, nor should the inherent food industry gases regulation.

In fact, food additives are highly regulated by European entities, in order to assure the gases used comply with specified criteria. Both oxygen and carbon dioxide must be produced in accordance with standardized regulation in the food industry, in particular ISO 22000 and FSSC 22000 (Food Safety System Certification) [37].

### 2.2.9 Comparative between major industrial oxygen applications in Portugal

In this section, a comparative is made regarding the 4 major industrial oxygen consumers in Portugal, namely glass furnaces, the iron making industry, pulp bleaching and wastewater treatment.

The Portuguese national paper industry reported that the production of pulp for paper production in 2019 was equal to 1.6 million tonnes, with a decrease of 1.9% compared to the year before [38].

For the iron making sector, the Portuguese foundry association was responsible for 90% of iron and steel metal production in Portugal. Figure 19 shows the metal production (in tonnes) in Portugal for the years of 2015, 2016 and 2017 [39]. For calculations purposes, an average value of 140 000 tonnes/year will be considered, which accounts for the sum of both grey/nodular iron and steel production for the year of 2017.

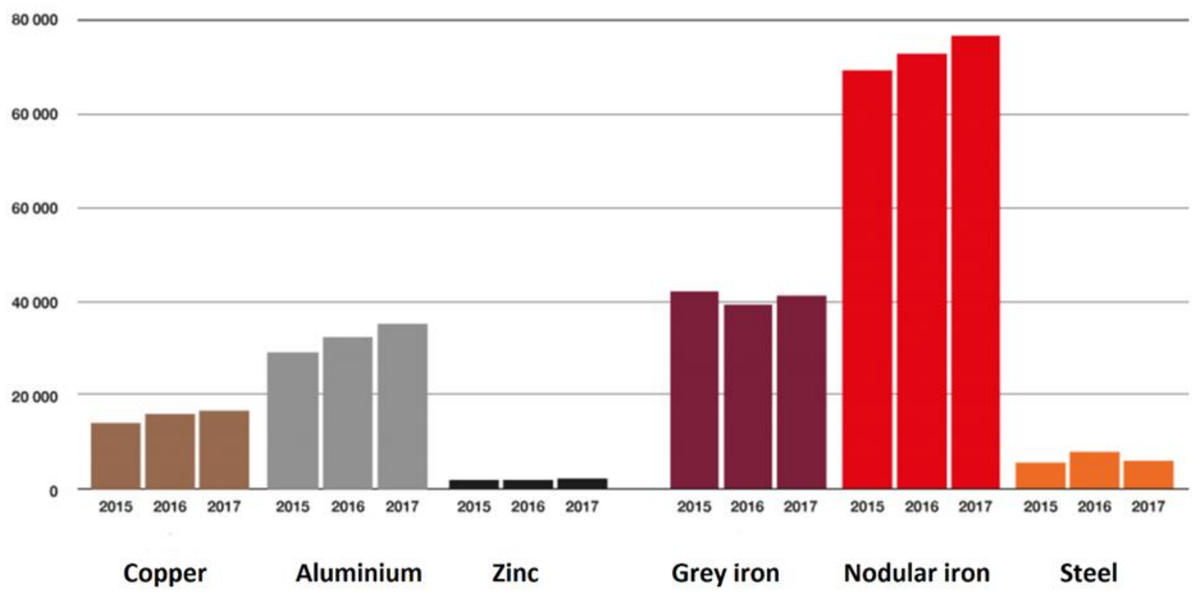


Figure 19 - Metal production in Portugal (in tonnes) (Adapted from the Portuguese foundry association [39])

Furthermore, Portuguese glass companies which integrate the European Packaging Glass Federation are responsible for the production of around 16 million bottles, flasks and jars, in 6 distinct factories, located in Vila Nova de Gaia, Figueira da Foz, Marinha Grande and Amadora. With 16 furnaces being used for glass melting, a total amount of 1.5 million tonnes of glass is produced annually in these facilities [40].

Lastly, regarding wastewater treatment facilities in Portugal, a total of 560 884 $m^3$ of wastewater was treated in 2009, which is a significant increase compared to 1991, where only

135 713 $m^3$ of wastewater have undergone treatment. In terms of untreated wastewater in Portugal, the opposite relation was recorded. In fact, the total amount of unprocessed water decreased from 236 983 $m^3$ in 1995 to 16 827 $m^3$ in 2009 [41].

Based on the state of the art discussed in this study regarding the major industrial oxygen consumers, the following assumptions are made:

- For pulp bleaching, an average consumption value of 45 kg $O_2$/tonne is assumed, which comprises both delignification and bleaching processes [28].
- Consider and oxygen demand for oxygen blast furnaces of 435 kg per tonne of steel produced [26].
- Assume for traditional blast furnaces a consumption of 162 kg of oxygen per tonne of steel [26].
- The oxygen demand for the oxygen combustion furnace is about 400 kg $O_2$/tonne of glass [10].
- An average oxygen consumption of 50 kg $O_2$/ tonne of water for oxygen activated sludge processes for wastewater management [28].

Figure 20 shows the oxygen consumption for these applications mentioned above, in kg of $O_2$ per tonne produced. Considering theses reference values, the total oxygen demand (in thousands of tonnes) in Portugal for each of these industries can be estimated. In fact, figure 21 underlines a promising demand for the Glass production in Portuguese territory. It is noteworthy to understand that currently most glass furnaces use air-blown combustion. However, as described in this study, oxygen combustion has many advantages, namely an energy consumption reduction and a decrease in both $NO_x$ and $CO_2$ emissions. Therefore, as industrial oxygen prices decrease due to mass production via water electrolysis, and also taking into account the rising carbon taxes, oxygen combustion is very promising for future glass melting processes.

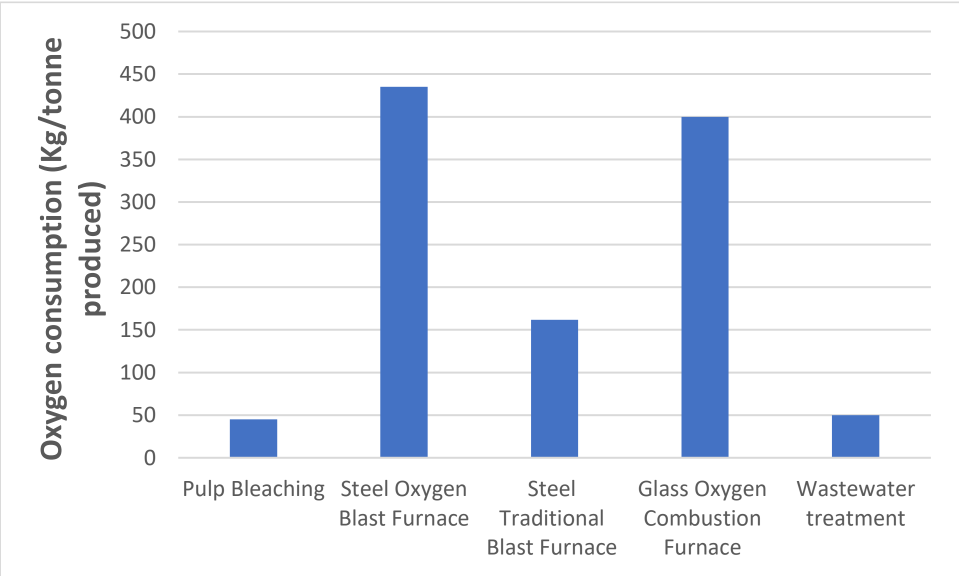


Figure 20 - Oxygen consumption for the highest potential consumers of industrial oxygen in Portugal (kg/tonne)

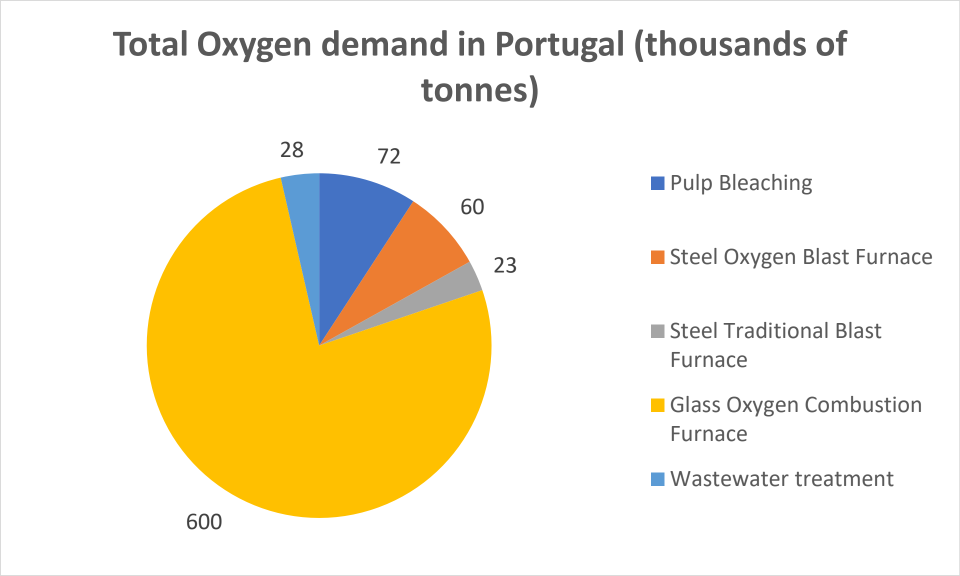


Figure 21 - Estimation of the total oxygen demand (thousands of tonnes) for Portugal

Moreover, a comparison is made regarding the industrial oxygen sales potential for Portugal (in millions of euros) considering and average oxygen selling price of 100 ad 150 €/tonne [8], [11] (figure 22).

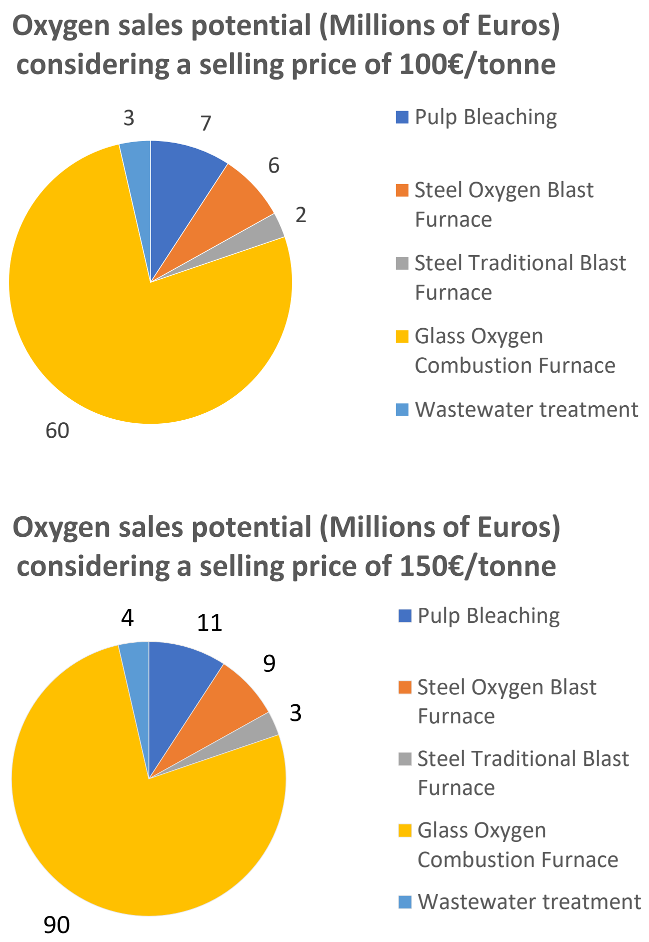


Figure 22 - Industrial Oxygen revenues potential (in millions of euros)

These locations can both leverage from water abundancy for the electrolysis process. Not only the fact of being located on the Atlantic coastline of Portugal, but also the possibility of using water from existing rivers, thus not requiring costly desalination processes (Douro river for the case of Vila Nova de Gaia and Mondego river in Figueira da Foz). The figure 23 illustrates the evolution of the volume stored by river basin from 2018 to 2020, in millions of cubic meters [42](figure 23).

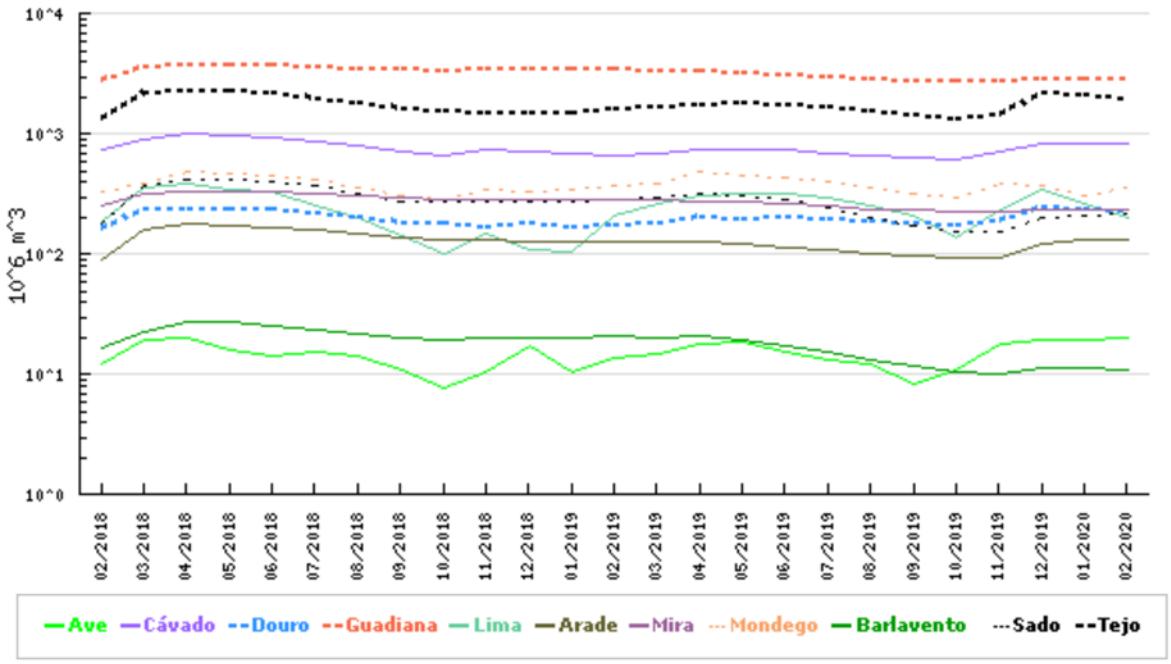


Figure 23 - Evolution of the volume stored by river basin (millions of cubic meters) (Source: Report on Storage in Reservoirs of Continental Portugal [42])

As it can be seen, both rivers present significant quantities of volumes stored, between 200 and 600 million cubic meters of water.

In addition, green hydrogen has also very interesting applications in these locations, namely for Power-to-Gas applications. Figueira da Foz has a natural gas combined cycle powerplant called "Lares" with 826 MW installed capacity, whereas Vila Nova de Gaia also has a natural gas powerplant of 990 MW called "Tapada do Outeiro"[43]. Storage and transportation concerns could be easily improved since green hydrogen could be directly used as a synthetic natural gas. Such syngas could be primary used in the gas turbine to generate electricity. In fact, the infrastructure of the combined cycle plant already exists, as well as the natural gas grids for synthetic natural gas injection.  Also, the implementation of electrolysers in the coastline could directly promote Portugal as an exporting country for compressed or liquefied hydrogen and oxygen tanks to the rest of Europe. This would be translated into a significant reduction in the final cost evaluation of the plant. Oxygen, on the other hand, could be directly used as a high purity by-product for the existing glass factories in these locations, reducing the payback period of the electrolysers, thus increasing its economic feasibility.

Vila Nova de Gaia location could also benefit from a new project developed by CaetanoBus in their factory in Ovar, regarding electrical buses incorporated with hydrogen fuel cells technology [44]. This project, called H2 City Gold, aims to decarbonize the public transportation sector, relying on 5 hydrogen tanks, with a total maximum capacity of 37.5 kg, and a 60 kW fuel cell. Such Portuguese manufacturer has already targeted an annual production of 100 $H_2$ buses, which represents a total of 3750 kg of hydrogen base consumption plus investing in recharging points [45]. In fact, green hydrogen production in such location, would decrease the costs related to hydrogen transportation and promote Portugal as a pioneer in the vehicle electrification market.

Moreover, apart from the glass industry as an oxygen by-product consumer in Figueira da Foz, other industries are worth being mentioned, in particular the pulp bleaching sector. “The Navigator Company”, one of the main papermaking companies in Portugal, relies essentially on 4 factories for the manufacturing process, located in Cacia, Setúbal, Vila Velha de Ródão and Figueira da Foz. In fact, the latter has a maximum production capacity of around 1.37 million tonnes of paper annually, including bleached eucalyptus pulp as well as uncoated printing and writing paper [46]. “Altri”, a major European company in the pulp industry, has 3 pulp and paper mills in Portugal, namely “Celtejo”, “Caima” and “Celbi”, which together account for an annual nominal production over 1 million tonnes. Interestingly, “Celbi” is also located in Figueira da Foz, and is has an installed capacity around 800 thousand tonnes annually of Bleached Eucalyptus Kraft Pulp (BEKP) [47]. Furthermore, British company “DS Smith” recently acquired a pulp mill in Viana do Castelo, located in the northern region of Portugal, with a reported production capacity around 425 thousand tonnes annually of paper pulp [48]. Besides, since commonly large pulp and paper industries have their own wastewater treatment facilities to assure regulatory compliance, by-product oxygen could also be directly used for sludge treatment processes.

In terms of renewable energy to power the electrolyser, two alternatives are suggested, both depending on wind energy due to the highest installed capacity in these locations. The first alternative depends on energy surplus of already existing wind farms. Figure 24 shows the wind sector distribution in Portugal in December 2018, in MW of installed capacity [49](figure 24).

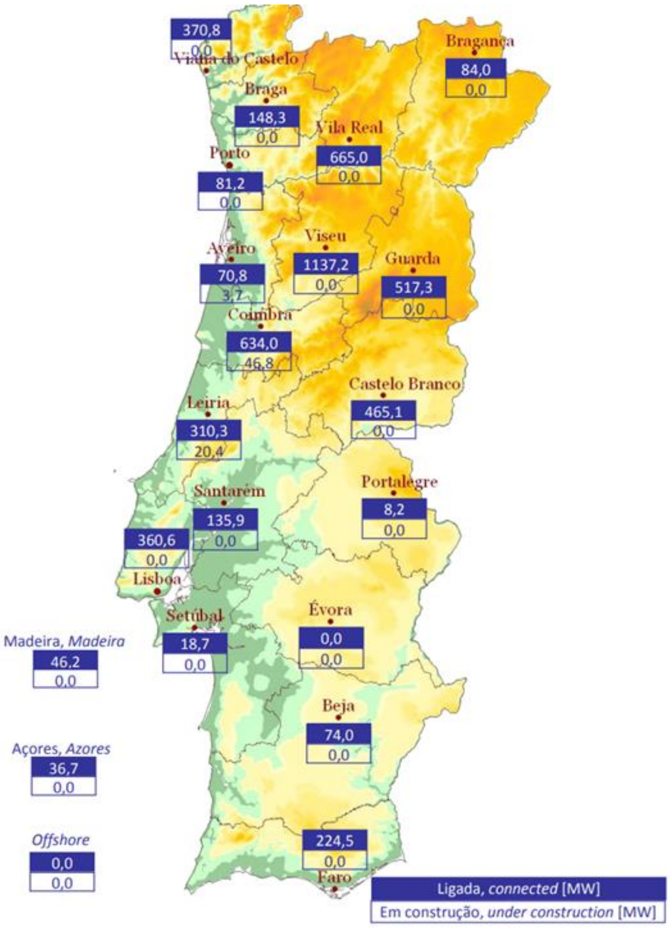


Figure 24 - Installed capacity per district and autonomous region 2018 (MW) [49]

As it can be seen, for the case of Vila Nova de Gaia, wind energy surplus could be brought from the nearest substations with sizable renewable energy production, such as from Viseu, Vila Real and Viana do Castelo, which together account for around 2173 MW of installed capacity.

On the other hand, as for the implementation of green hydrogen production in Figueira da Foz, the energy surplus for the electrolysis could be provided from wind farms located in Coimbra, which represents an amount of 689.8 MW of installed capacity.

The second alternative relies on floating wind turbines, a technology which has been developed in these recent years in a pilot project called “Wind Float Atlantic”, carried out by the Portuguese company EDP located on the coast of Viana do Castelo [50]. In fact, the Atlantic Coast has and abrupt depth variation as the distance from the coastline increases. Therefore, contrarily to the North Sea, conventional monopile offshore wind turbines foundations are impossible to implement in the Portuguese coast. The possibility of floating technology enables Portugal to expand its wind energy penetration in the national market by integrating offshore wind assets, in particular for further water electrolysis powering. This project has been successfully implemented with a total of 25 MW installed capacity consisting of 3 platforms of 8.4 MW each [50]. As such technology becomes more mature in the future, it might solve the offshore issue for Atlantic Coast zones, being a promising pathway for green hydrogen production.

Another possibility to power the electrolysis could be by solar energy. In 2020, solar panels represented a 13% market penetration of the total renewable energy sources installed capacity in Portugal, compared to a 36% market share of wind energy (figure 3 [3]). Nevertheless, according to this same study performed by the consultant Deloitte, both energy sources will have an identical market share around 30% by 2030, in order to accomplish the targets by the National Energy and Climate Plan.

In fact, for the case of solar energy in Portugal as the electrolysis power source, the South region of the country has higher interest, since it has considerably larger sun exposer, up to 1900 kWh of solar irradiance per square meter, per year [51]. A promising location of such plant implementation is in Sines, which can leverage from the already existing natural gas pipeline connected to the transportation national grid. The European union is already promoting the implementation of a project called “Green Flamingo” in such region, based on a 1 GW solar powered electrolysis capacity. Another advantage of this project is the opportunity to ship directly compressed hydrogen from the port of Sines to Rotterdam and ultimately, to the rest of the countries in Europe. As for the possible by-product oxygen industry consumers in Sines, local metal treatment and surfacing industries can directly benefit from it [52]. In addition, Sines municipality covers a total of 3 wastewater treatment facilities, located in Ribeira dos Moinhos, Porto Covo and in Bairro Novo da Provença [53], which are a significant oxygen consumer for sludge treatment processes, as previously shown in figure 20.

In order to further increase solar penetration in the Portuguese market, many auctions have been proposed by the government. The most recent incentive regarding such renewable source will be launched in the middle of 2021 and consists in the instalment of floating photovoltaic panels on dams, taking advantage of the space and potential of water mirrors. Furthermore, such alternative would prevent the overoccupancy of land, and minimizing the natural water evaporation.

According to calculations done by the Portuguese Ministry of the Environment, if 20% of the area of the country's 50 largest dams was to be occupied by photovoltaic panels, solar production would reach 7.6 GW, thus meeting the 2030 solar market share target [54].

In that sense, for the present scenario being discussed in this study, the “Alqueva” dam in Portugal is assumed as a worthwhile option, being the biggest water reservoir in Iberia. Portugal´s major energy supplier, EDP, already secured an investment of 4 MW installed capacity of a floating solar farm [55]. Even though such installed capacity is minor for green hydrogen production purposes, it represents a viable alternative once such technology becomes mature and fully developed.

In conclusion, further studies should be performed in order to assess such possibility, by discussing which renewable energy source might be the most appropriate for a green hydrogen electrolyser plant in these locations mentioned above.

## 2.3 Medical Oxygen applications

### 2.3.1 Medical Oxygen consumption in the World

Oxygen is widely used for medical care, mainly used for the treatment of diseases related to chronic respiratory failure, which results in difficulty in breathing, severe fatigue and accelerate heart rate [56]. In fact, oxygen therapy is considered the medical treatment with the highest oxygen demand. Since oxygen is regarded as a medicine, the environment in which it is produced is highly regulated and supervised. In order to comply with such regulations, medical oxygen is produced in independent air separation plants and further transported in cryogenic storage vessels. For hospitals with elevated oxygen consumption rates, apart from the conventional equipment required for oxygen transportation, such infrastructure might even include special instruments for medical air production [57].

Nevertheless, with the continuous increase in medical oxygen demand, other technologies are being studied for oxygen production, namely pressure swing adsorption and by-product oxygen from electrolysis. The latter is very promising, due to the rising demand for green hydrogen for the energy industry. Furthermore, such reutilization of oxygen with very high purity levels could both reduce the green hydrogen production cost and the medical oxygen market value.

A study was performed prior to the Covid 19 pandemic in 2018, considering a sample of 12 Spanish hospitals in order to quantify the medical oxygen consumption, and how it would vary according to the existing floor area and number of beds occupied by patients with respiratory diseases [57]. For comparison purposes, an inquiry was performed in Mexico, to appraise the oxygen consumption according to hospital size. In fact, for 61% of the buildings considered, less than 1500 $m^3$ (2006 kg) of oxygen were consumed each month. For the case of large size hospitals, which accounts for 28% of the sample studied, a value of 3000 $m^3$ (4011 kg) was assumed. Lastly, the medium size buildings registered an oxygen consumption between these values presented, corresponding to 11% of the sample surveyed [57].

Furthermore, relatively to oxygen transportation in cryogenic vessels, three main dimensions are normally used, depending on the medical gas demand. Typically, a 50 Litre cylinder (B50) contains around 10.60 $m^3$ (14 kg) of oxygen. An intermediate capacity of a 10 Litre cylinder (B10) accommodates 2.12 $m^3$ (2.8 kg) of oxygen, whereas the minimum size of a 5 Litre cylinder (B5) contains around 1 $m^3$ (1.3 kg) of oxygen [57].

According to Chaparro et al. [57], a correlation was obtained between the average annual medical gas consumption and the useful floor area of the hospital, given by the expression:

$$C = 0.0002\, A^{1.3126} \tag{5}$$

Where *C* represents the average annual oxygen consumption, in $Dm^3$ and *A* represents the useful floor area, in $m^2$. Figure 25 [57], shows a R-squared value of 0.7937 for the present correlation, which is an adequate approximation.

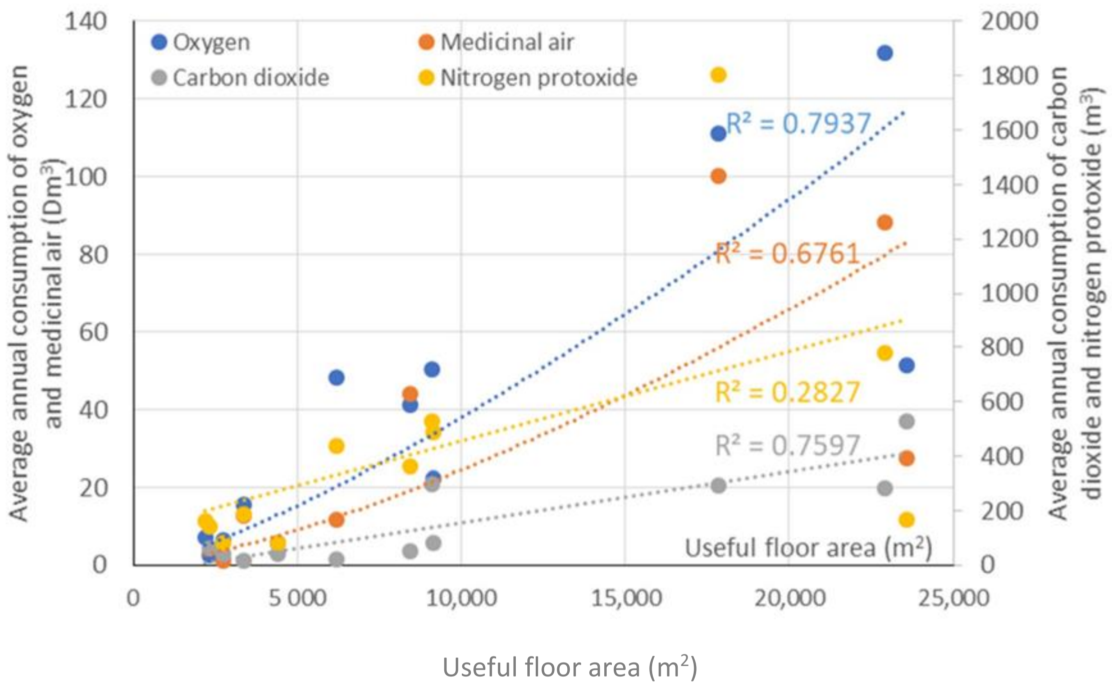


Figure 25 - Medical gas consumption as a function of the useful floor of the hospital [57]

In terms of the number of beds occupied, this same study [57] concluded that there was an even more accurate correlation (with a R-squared value of $R^2$=0.9551) with the average annual oxygen consumption, given by the following expression:

$$C = 0.0083\ B^{1.8140} \tag{6}$$

where B represents the number of beds occupied. Such correlation is demonstrated in figure 26 [57].

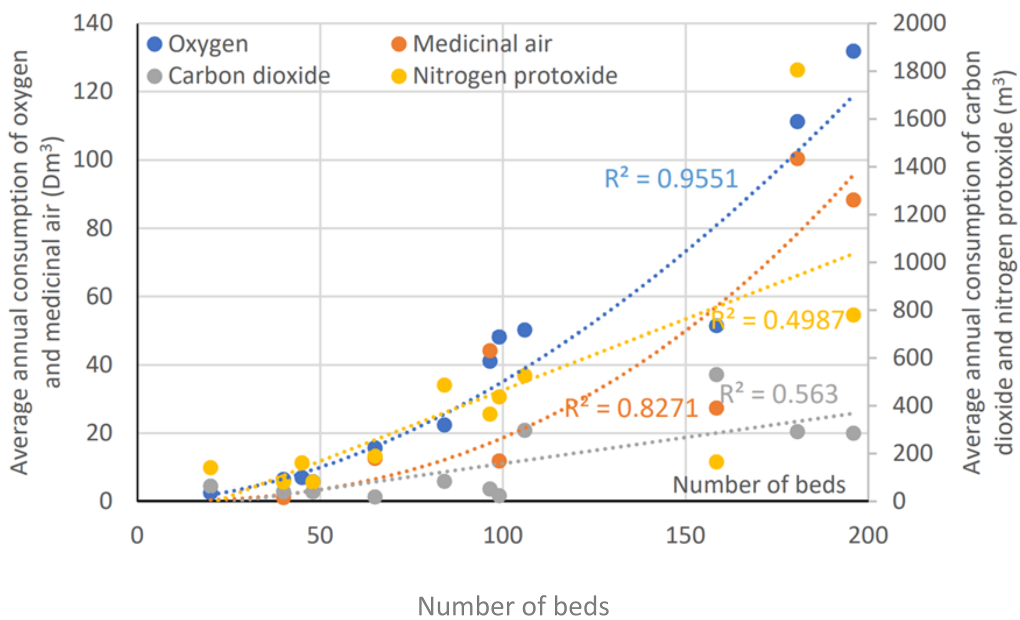


Figure 26 - Medical gas consumption as a function of the number of beds occupied [57]

In fact, a value of 350 $m^3$ (468 kg) of oxygen was assumed per hospital bed per year [57].

In terms of medical oxygen cost, some factors can influence its variation, namely whether the oxygen is delivered from an external supplier in cryogenic vessels or produced on-site in the hospital facilities. For the case of pressurized oxygen cylinders, oxygen price per unit volume at standard temperate and ambient conditions was estimated, based on correlations from an extensive literature review. In fact, medical oxygen costs in Spain and in Japan were analysed. For the Iberian country, a price of 1 €/$m^3$ (1.342 €/kg) of oxygen was assumed for the 50L Barrel and 5 €/$m^3$ (6.7 €/kg) for the case of B10. Note that if liquid oxygen in bulk is considered, its price is significant less, around 0.5 €/$m^3$ (0.675 €/kg) [57]. In Japan, however, costs are slightly high, in particular for the case of pressurized cylinders used as a transportation medium. Prices can vary from 0.48 €/kg to 20.56 €/kg, depending on the total oxygen demand and also the transportation and storage medium used [10]. For the Japanese scenario, a gas oxygen cylinder from 500 L to 1500 L can cost around 44 €/kg whereas for larger quantities of a 6000 L cylinder, the cost is estimated to be around 5.3 €/kg [10]. Liquid bulk oxygen, which is the most considered for hospitals and medical care facilities, has a price around 1.18 €/kg [10].

### 2.3.2 Impact of Covid 19 pandemic on the medical oxygen demand

Covid 19 pandemic affected drastically the medical oxygen demand in hospitals, since this disease attacks severely the respiratory system as well as reducing the patient´s blood oxygen levels. Thus, challenges have been encountered regarding providing a continuous oxygen supply and further storage and distribution, in particular in under development countries located in Africa and Asia. Therefore, Covid 19 required some modifications in the oxygen distribution. In particular, since the oxygen demand surpassed its supply, some hospitals decided to build onsite oxygen generators, under the strict production environment which is imposed by health authorities, assuring purity levels between 93 and 95% [58].

A typical child with pneumonia spends around 3 to 4 days hospitalized, consuming between 4 and 8 $m^3$ of oxygen during that period [58]. Nevertheless, an adult patient diagnosed with Covid 19 is assumed to consume twice as much oxygen than a non-Covid adult patient with other respiratory diseases. From all patients who contract Covid 19, roughly 14% are admitted to a hospital [59].

Depending on the severity of the patient´s respiratory failure related to Covid 19, oxygen therapy can be applied with different flow rates ranges. For the case of children, low doses of 1-2 L/min are given. In adults, flow rate ranges can vary from 5 L/min delivered by nasal cannula, an intermediate value of 6 to 10 L/min using venturi masks or 10 to 15 L/min in more critical patients via masks with reservoir bags [60].

According to a study performed from a sample of 133 patients infected with Covid 19, admitted in the RWTH Aachen university hospital [59], 57 of them required additional oxygen therapy, without needing to be admitted to the Intensive Care Unit. In fact, such patients were reported to require oxygen assistance for an average period of 8 days (5 to 13 days).

Based on these results, a comparison between the oxygen demand can be performed regarding Covid 19 patients and the type of oxygen therapy they should require, as shown in figure 27.

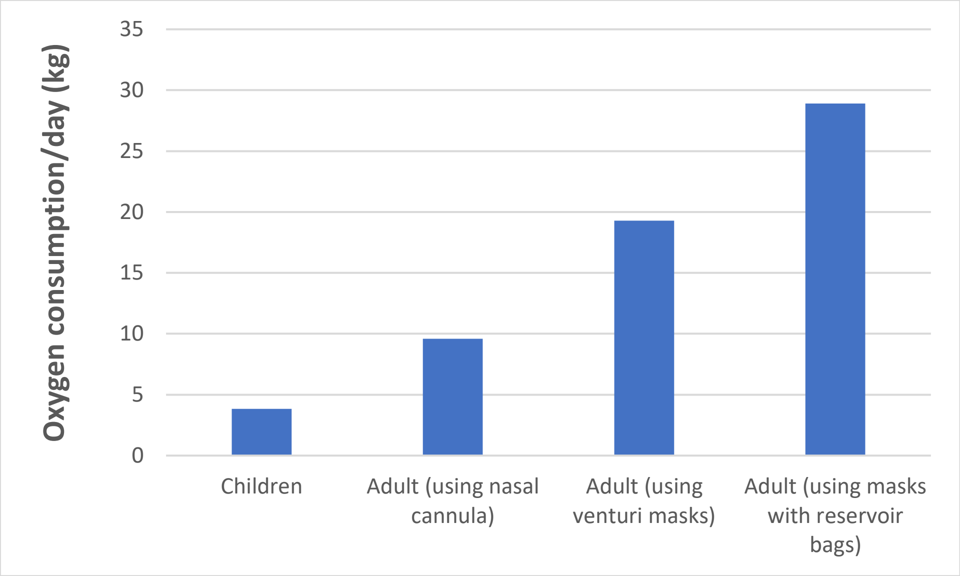


Figure 27 - Covid 19 patients Oxygen consumption per day (in kg), RWTH Aachen university hospital, 2019.

In terms of medical oxygen expenses related to Covid 19 pandemic, considering a reference price value of 0.675€/kg for liquid bulk oxygen and an average 8-day period of hospital stay [59], the following analysis can be performed as shown in figure 28.

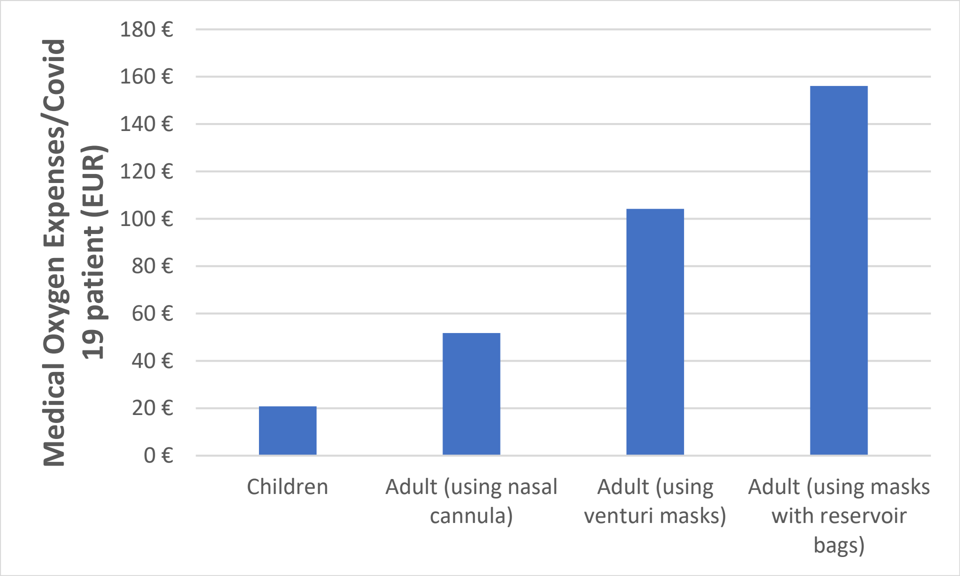


Figure 28 - Medical Oxygen Expenses (in Euros) per Covid 19 patient requiring oxygen therapy, in average 8-day period, RWTH Aachen university hospital, 2019.

As it can be seen, medical oxygen cost represents around 50 € up to 160 € per each Covid 19 adult patient who needs oxygen therapy, considering an 8-day hospitalization period.

Overall, medical oxygen represented in 2019 a market size of about €4.25 billion and is expected to rise up to €6.8 billion in oxygen sales by the year of 2026 [48]. For this reason, alternatives to the conventional cryogenic vessels should be properly addressed, with special focus on green hydrogen electrolysis, which assures the required oxygen purity levels. However, the main barrier of electrolysis by-product oxygen for medical use is the regulations associated with the production environment. In fact, apart from representing an additional cost to the plant, these safety standards may vary according to the health ministry of the country where the plant is being installed.

Furthermore, by diversifying the oxygen suppliers as well as the adjacent technology being used, governments would be able to better address the monopoly of the main gas companies regarding oxygen supply. Thus, different medical oxygen pathways would both reduce cost upsurges and incoherent supply of such a high market value gas.

### 2.3.3 Medical Oxygen consumption in Portugal

According to information provided by Infarmed, Portugal´s health entity regulator, an assessment was made in order to quantify the medical oxygen consumption in the main hospitals in Portugal, as well as to analyse its economic market value [61].

For further calculations regarding oxygen consumption in Portugal, medical oxygen costs were assumed to be very similar to those in Spain. In fact, liquid bulk oxygen was estimated to represent the same cost of 0.68 €/kg [57]. Furthermore, for the case of pressurized oxygen vessels, an average price of 2.38 €/kg was assumed for the B50 size whereas a higher value of 8.8 €/kg was considered for the B05 cylinders. Thus, medical oxygen in Portugal can be assumed to vary from around 680 €/tonne (for the case of bulk liquid oxygen) and 8800 €/tonne (if B05 tanks are considered) [10],[57]. It is noteworthy to underline that such prices are applied to the continental territory. In the archipelagos of Azores and Madeira, liquid bulk oxygen cost can be three times much higher than the values presented in this study.

Figure 29 presents the evolution of the medical oxygen expenses (in Euros) from 2012 to 2019, considering a total amount of 45 hospitals in Portugal.

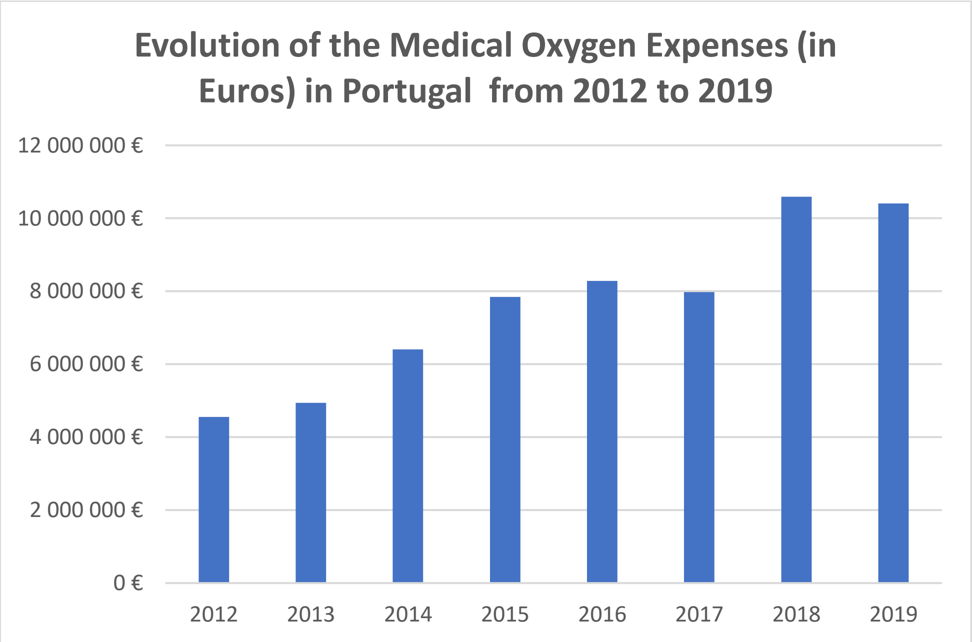


Figure 29 – Evolution of the medical oxygen expenses (in Euros) in Portugal from 2012 to 2019

In fact, figure 29 shows an increasing tendency regarding medical oxygen expenses throughout the last years from around 4 million euros in 2012 up to 10 million euros in 2019. For calculation purposes, a total value of 8 281 160 euros was assumed, which represents the medical oxygen consumption of the year of 2016, equivalent to around 12 359 940 kg of oxygen consumed, considering liquid bulk oxygen selling price [57].

Figures 30, 31 and 32 express the medical oxygen expenses depending on the weight percentage of the oxygen consumption per hospital. In this manner, the analysis was carried out considering the national hospitals with the highest oxygen consumption (with a weight percentage between 7.1 and 13.3%), hospitals with an average oxygen consumption (with a weight percentage between 0.8 and 1.1%) and the hospitals with the lowest oxygen consumption in Portugal (0.01 to 0.08% weight percentage), respectively.

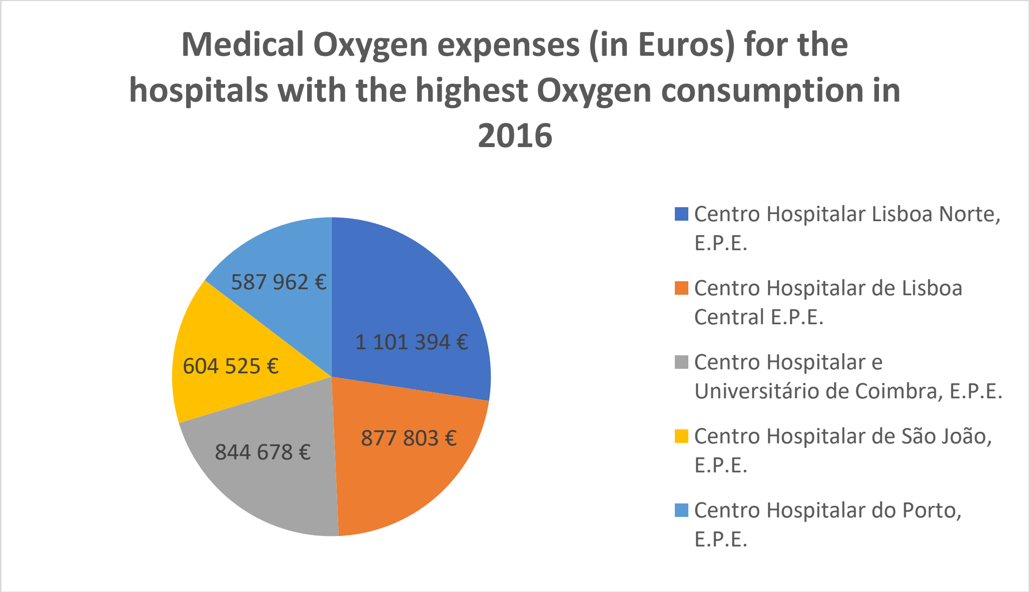


Figure 30 - Medical oxygen expenses (in Euros) for the Portuguese hospitals with the highest oxygen consumption in 2016

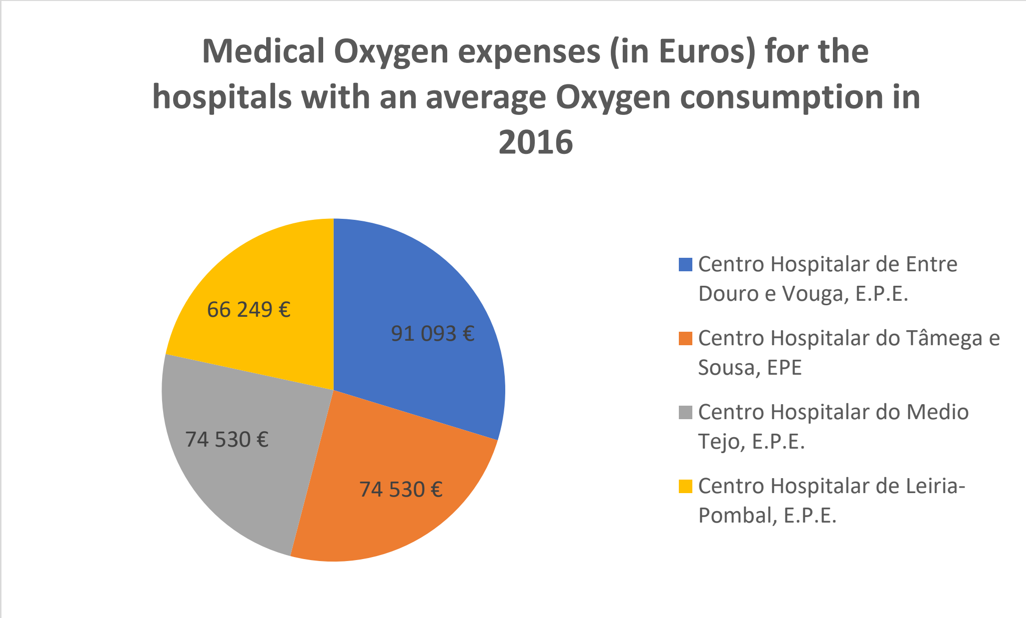


Figure 31 - Medical oxygen expenses (in Euros) for the Portuguese hospitals with medium oxygen consumption in 2016

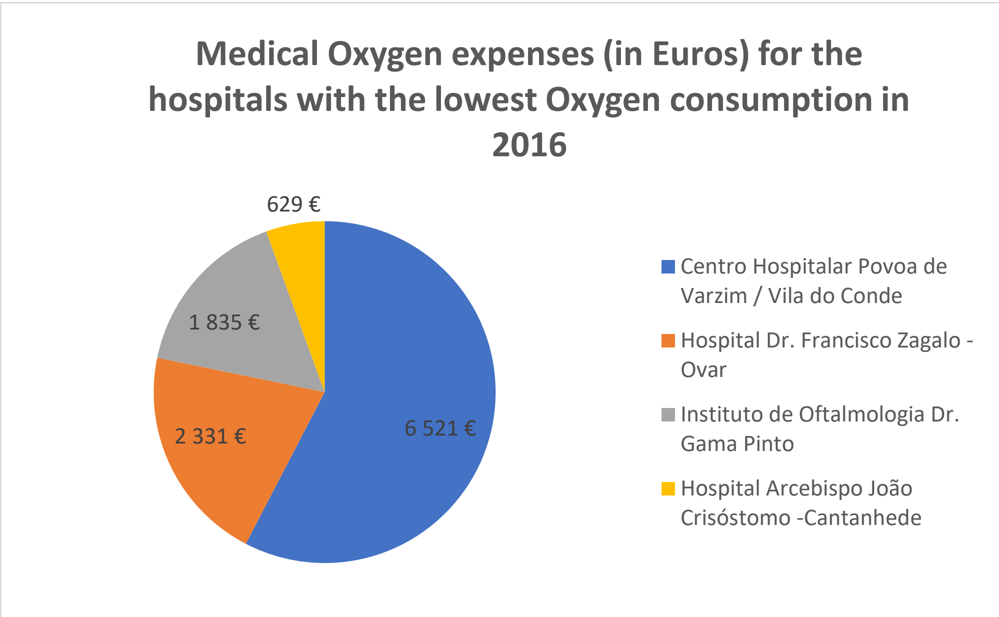


Figure 32 - Medical oxygen expenses (in Euros) for the Portuguese hospitals with small oxygen consumption in 2016

As it can be seen, medical oxygen expenses vary drastically with regard to hospitals size and weight percentage in oxygen consumption. Therefore, an average annual expense value for medical oxygen can be assumed around 2830 € for a small hospital, 76 600 € for a medium hospital with an average oxygen consumption and ultimately, 803 273 € for the case of a big hospital with high oxygen consumption.

For the case of the Portuguese hospitals with the highest oxygen demand in 2016, the figure below exhibits an estimation for the total oxygen consumption (in tonnes) per hospital.

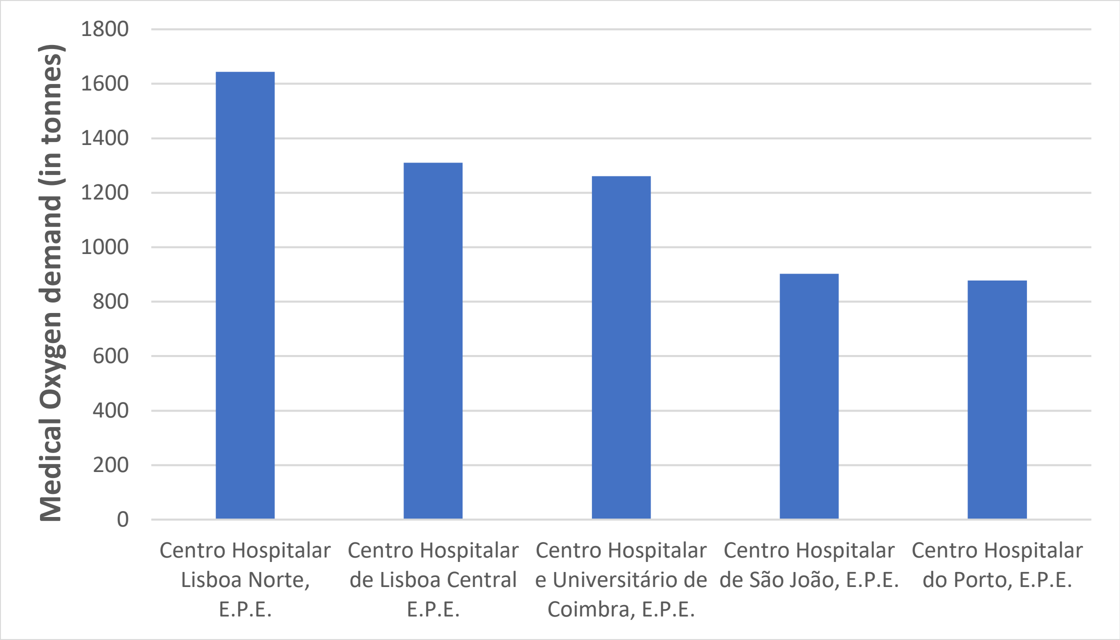


Figure 33 – Estimation of the medical oxygen demand (in tonnes) for the Portuguese hospitals with the highest oxygen consumption in 2016

It is worth highlighting the oxygen consumption for the Portuguese hospital "Centro hospitalar Lisboa Norte, E.P.E.", which is around 1.6 million kg, considering liquid bulk oxygen. In reality, not all oxygen is delivered in bulk. Assuming that part of it would be delivered in B05 and B50 vessels, which have a relatively higher selling price, the estimations of the oxygen consumption per hospital would be smaller.

Moreover, a study was performed in order to correlate the total medical oxygen consumption in all Portuguese hospitals with the number of beds occupied, according to information provided by Infarmed [62].

The polynomial trendline obtained has a R-squared value of 0,5794, which is significant less compared to the Spanish hospitals scenario [57]. This study estimated an average value of 379.4 kg of $O_2$ per hospital bed occupied, slightly lower than the value reached of 468 kg $O_2$/ bed regarding oxygen medical consumption in Spain [57].

In fact, such deviation from Portuguese and Spanish scenarios regarding the actual medical oxygen consumption per hospital bed [57],[62] can be related to some aspects worth being mentioned. For instance, for the year of 2016, which included a total of 35037 beds in Portugal's hospitals [62], there is a deviation of 33% from the Spanish correlation, assuming bulk liquid oxygen selling price. Such computed deviation was only around 5% for the year of 2018, assuming 35429 beds and 11% for 2019, where 36913 beds were registered in all Portuguese hospitals [62]. Some factors which might be directly involved with such error are the fact that medical oxygen selling price varies according to market demand and the way it is delivered to hospitals (bulk, B05 and B50 tanks), and also considering that there are pipeline losses from where oxygen is stored until its final consumer. In addition, it is important to highlight that the Spanish scenario only considered a range until 200 beds. Thus, a relative error is prone to occur, since hospitals with different dimensions are being compared. Note that for the case of a large Portuguese hospital, such as Santa Maria, more than 1000 beds were considered (five times larger than the Spanish base case).

For the year of 2020, medical oxygen consumption in Portugal was highly affected due to Covid 19 pandemic. Considering roughly 1 year period from mid-March 2020 to the beginning of April 2021, around 822 thousand cases were registered in Portugal [63]. In fact, such impact of the pandemic alone is estimated to represent an oxygen consumption of 7 615 008 kg in 2020 [59], [60]. In terms of oxygen expenses per year related to the pandemic, its value is reported to vary from around 5 million euros (considering bulk liquid oxygen) up to 67 million euros, if all oxygen had been delivered via B05 tanks. In fact, the sudden rise in the oxygen demand followed by the lack of such stored gas availability in hospitals has proven to be a major issue for healthcare entities, forcing them to broaden oxygen´s production and transportation alternatives, some of them more expensive. Therefore, considering oxygen consumption for Covid 19 patients, in addition to the average annual demand for traditional respiratory diseases, the oxygen demand in 2020 increased by 62% compared to 2016, and by 50% in relation to 2019.

Another key insight in this study is the oxygen consumed in home care applications regarding oxygen therapy. In fact, based on information provided by Infarmed and the Portuguese national institute of statistics, as well as from previous studies regarding medical hospital consumption [10], [61], [62], [64], this work estimates that Portuguese hospitals only represent around 50% of the total medical oxygen consumed. The other 50% accounts for patients with respiratory diseases which require oxygen therapy at home. Oxygen cylinders for homecare purposes can be static or portable. For the first case, typically a 10 L cylinder (2 $m^3$) is commercially used in addition to an oxygen concentrator, being responsible for filtering the oxygen from the air, which is then consumed by the patient in need via cannula or venturi masks. The 10 L oxygen cylinder enables the patient to continue to consume oxygen in a scenario where an electricity cut or a machine failure might occur. An average cost of 6.7 €/kg for the B10 cylinder is considered for the Portuguese medical gases [57]. Portable oxygen cylinders for home care applications have normally 2 sizes, 1 L and 2 L depending on the patient being a children or adult [65]. These cylinders are more suitable for patients who still have active lifestyles, increasing mobility and providing independence. A standard 2 L cylinder is estimated to cost around 9 €/kg, based on correlations from the Spanish and Japanese scenarios discussed in previous studies [10], [57].

Thus, for the year of 2019, which is the last year assumed prior to the Covid pandemic crisis effect in oxygen peak demand, home care oxygen consumption represented a estimation value of 1 326 025 kg, considering and average oxygen selling price of 7.9 €/kg depending on the cylinder size and purpose (stationary or portable application) [61], [62].

Below is presented the estimated correlation between the pressurized oxygen cylinder size, in Litres, and the respective selling price, in €/kg (figure 34 [10], [57], [62]). Note that the chosen exponential trendline exhibits a very well-established behaviour, with a R-squared value of 0.9905.

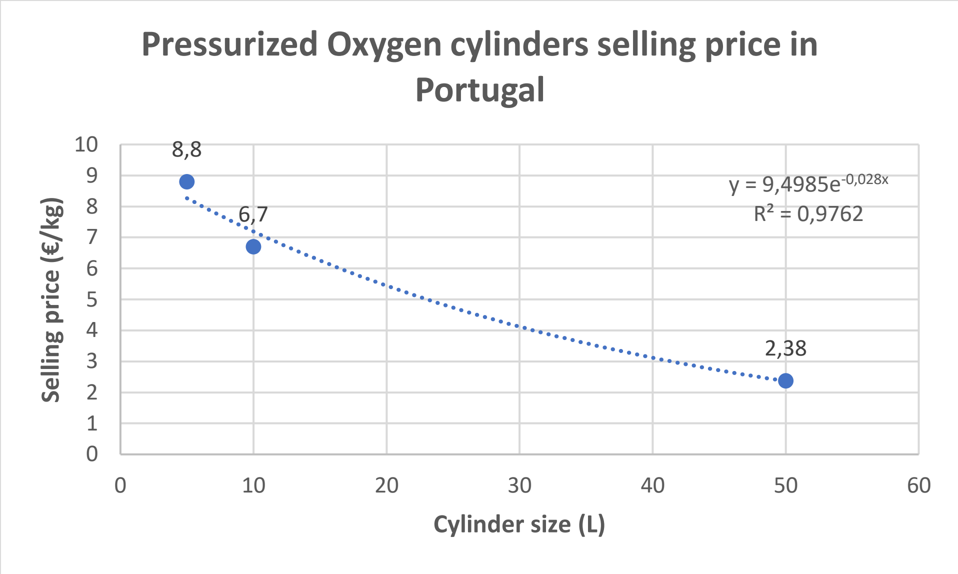


Figure 34 – Estimated Pressurized Oxygen cylinder selling price in Portugal

In conclusion, medical oxygen is reported to represent a very interesting market value in Europe, and in particular, in Iberian territory. Moreover, considering the promising increase in oxygen demand over the years, with special emphasis on the pandemic period and the increase of the lifetime expectancy, associated respiratory diseases, it is essential to investigate other alternatives of producing and transporting medical oxygen, thus assuring constant availability of stored gas in hospitals. In this manner, by-product oxygen from water electrolysis becomes a valuable alternative, being a very competitive option with the current cryogenic technology in terms of oxygen purity.

## 2.4 Green Hydrogen

### 2.4.1 Water electrolysis technologies

Water electrolysis separates both molecules of hydrogen and oxygen from water, through an electrochemical process. While requiring electricity from renewable energy surplus, 9 litres of water can be used to produce 1 kg of $H_2$ and 8 kg of oxygen as a by-product, which can have very important applications in the industrial and health sector as already explained in this study. Currently, green hydrogen accounts for less than 0.1% of the total hydrogen produced worldwide. Due to its high purity, its market applications include particular electronic components [66]. Nevertheless, green hydrogen shows tremendous further applications, if a large-scale production is obtained. In fact, 617 million cubic metres of water would be needed to produce around 70 million tonnes of $H_2$ by electrolysis, which represents the present hydrogen demand for the varied industrial sectors. Thus, water electrolysis has a water demand 33% higher compared to grey hydrogen obtained from steam methane reforming (approximately 345 million $m^3$ of water for a total 52 million tonnes of grey hydrogen), but with no consumption of methane and no $CO_2$ emissions [66].

Nowadays, for obtaining green hydrogen from water electrolysis, 3 major technologies are under consideration, namely Alkaline Electrolysis Cells (AEC), Proton Exchange Membrane (PEM) Electrolysis Cells and Solid Oxide Electrolysis Cells (SOEC).

Alkaline electrolysers are the most mature and cost-effective technology in the market, since it is not composed by delicate metals. Furthermore, these electrolysers are mainly used for hydrogen production in the fertiliser and chemical industries [66]. Alkaline electrolyses was already during 40 years (from 20's and 60's) the dominant way of producing hydrogen, but the methane price drop a lot in the 50's and the steam methane reforming became dominant from the 60's until the present. For this reason, further sensitive analysis in this study will be performed considering alkaline cells. Nevertheless, there are some drawbacks worth mentioning, namely the low current densities required (0.2-0.5 $A/cm^2$) and moderate partial load range (20-40%) [9].

In order to overcome such obstacles, PEM electrolysis cells were introduced to the market based on a solid polymer electrolyte (SPE). Major advantages include higher current densities (superior than 2 $A/cm^2$) [9], gas purity and good cell efficiency. Another key leverage is the highly compressed hydrogen production (typically 30–60 bar without an additional compressor as opposed to 1–30 bar for alkaline electrolysers) [66], [67]. However, current costs are higher due to the expensive electrode catalysts (such as platinum and iridium) and membrane materials. In addition, reduced lifetime compared to alkaline electrolysers is also a major issue, as well as the design complexity due to higher pressure operation [66].

Ultimately, Solid Oxide Electrolysis Cells are the least mature technology in the market, however very promising for the future.

SOECs rely on relatively reduced cost ceramic materials as the electrolyte and operate at high temperatures up to 1000 °C [67]. Besides, great electrical efficiency is also an important advantage. A particular property of SOEC technology is the fact that it uses steam for the electrolysis process, which could be recovered from the waste heat of certain applications, namely power-to gas combined cycles [66]. Moreover, such electrolysers can be used in reverse mode behaving as fuel cells, meaning they would be a good solution both for hydrogen storage and to balance the peak demands in the electricity grid [66]. The fact that it can be used for co-electrolysis to obtain syngas consisting in hydrogen and carbon monoxide from electricity is also a promising pathway to reduce carbon emissions [67]. Still in laboratory development phase, such electrolysers are expected to be commercialized in a large scale in a near future, once researchers overcome its main obstacle, regarding material deterioration due to the high operating temperatures [67]. The higher temperature increases the speed of the interesting reaction but also the speed of some degradation materials reaction that will reduce the durability of the entire system.

Figure 35 and table 4 exhibit a comparison between the 3 technologies mentioned above and its main technical characteristics.

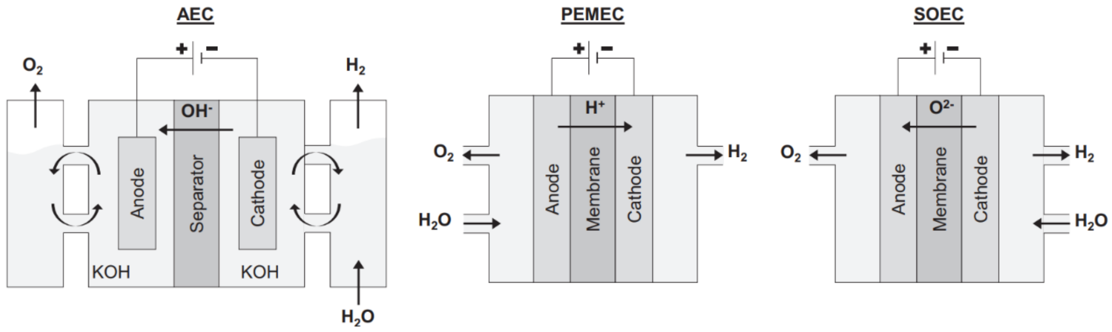


Figure 35 – Electrolysis cell technologies assemble [67]

Table 4 - Characteristics of the different electrolysis technologies

| **Characteristics** | **Alkaline electrolyser** | **PEM electrolyser** | **SOEC electrolyser** |
|---|---|---|---|
| Electrolyte [67] | Aq. potassium hydroxide (20-40 wt% KOH) | Polymer membrane (e.g. Nafion) | Yttria stabilised Zirconia (YSZ) |
| Cathode [67] | Ni, Ni-Mo alloys | Pt, Pt-Pd | Ni/YSZ |
| Anode [67] | Ni, Ni-Co alloys | $RuO_2$, $IrO_2$ | LSM/YSZ |
| Current density ($A/cm^2$) [67] | 0.2-0.4 | 0.6-2.0 | 0.3-2.0 |
| Cell voltage (V) [67] | 1.8-2.4 | 1.8-2.2 | 0.7-1.5 |
| Operating Temp.(°C) [67] | 60-80 | 50-80 | 65-1000 |
| Operating Pressure(bar) [67] | <30 | <200 | <25 |
| Gas purity (%) [67] | >99.5 | 99.99 | 99.9 |
| Electrical efficiency (%, Lower Heating Value (LHV), today) [66] | 63-70 | 56-60 | 74-81 |
| Electrical efficiency (%, Lower Heating Value (LHV),2030) [66] | 65-71 | 63-68 | 77-84 |
| Stack Lifetime (thousand operating hours) [67] | 60-90 | 30-90 | 10-30 |
| Capex (€/$kW_e$) [67] | 1000-1200 | 1860-2320 | >2000 |
| Maturity [67] | Mature | Commercial | Demonstration |

### 2.4.2 Green Hydrogen applications

Hydrogen is a widely used gas in the industrial sector, such as oil refining, steel production and also in the chemical industry, namely ammonia and methanol production. In fact, since all these industries are heavy $CO_2$ pollutants, green hydrogen will play a very crucial role in the energy transition period, while also contributing to reach a cost competitiveness target compared to existing conventional technologies. Moreover, hydrogen is also being targeted as a possibility to be mixed with natural gas for building heating purposes [68].

According to IEA [66], oil refining is the main hydrogen consumer, representing 33% of the current industrial hydrogen applications (38 Mt $H_2$/year). Other major consumers also have significant shares, with ammonia production representing 27% (31 Mt $H_2$/year), methanol production 11% (12 Mt $H_2$/year) and steel production via Direct Reduced Iron around 3% (4Mt $H_2$/year).

**Oil refining**

For the oil refining sector, currently more than 60% of the hydrogen used is produced via methane steam reforming [66]. Hydrogen is mainly used for hydrotreatment and hydrocracking processes and accounts for 20% of total refinery emissions (230 Mt$CO_2$/year)[66]. Existing impurities such as sulphur are removed via hydrotreatment. As climate concerns urges, regulators have announced stricter policies with a 2020 target of 40% less sulphur allowed at the end of the refining process compared to 2005 [66]. Hydrocracking is used to enhance residual oils into increased value products. The reminiscing hydrogen, which is not recovered to further processes, is burnt and released into the atmosphere.

The two main pathways to decarbonise such industry with an increasing demand are either Carbon Capture Storage technology or green hydrogen. In fact, retrofitting CCS units might be the most current competitive solution, since many refineries operate with natural gas from steam methane reforming process. Nevertheless, CCS implementation costs roughly 0.2 to 0.4 € per barrel, which is superior than carbon price levels around 0.083€ per barrel [66]. For this reason, unless there are some policy regulators to increase carbon costs, the refinery industry will continue reluctant to invest in CCS technology. As for the green hydrogen pathway, policy incentives are also vital in order to accomplish a competitive cost in comparison with conventional technologies.

**Chemical industry**

Ammonia and methanol production consume significant amount of hydrogen throughout its process. In fact, both chemicals contribute for notable carbon emissions, with a registered consumption of 270 million tonnes of fossil fuels in 2018 to produce its required hydrogen [66].

For the case of Ammonia, its main applications are in the fertilizing sector, namely for urea and ammonium nitrate. Typically obtained by the Haber-Bosch reaction, its carbon footprint would truly benefit from the implementation of green hydrogen via water electrolysis, since this process depends on great quantities of nitrogen and hydrogen as feedstock [68]. Furthermore, ammonia´s cost is highly correlated with green hydrogen production cost and, subsequently, renewables electricity cost. In Europe, an hydrogen price of 1.16 €/kg by 2030 would be enough to reach breakeven of clean ammonia compared to traditional technologies [68].

Methanol, apart from being used for solvent purposes, is essential for gasoline production from coal and natural gas [66]. Besides, it can also be transformed into olefins, such as ethylene or propylene, thus having a growing penetration in the plastics industry. Interestingly, some high performance plastics can be obtained from oil products without hydrogen as feedstock, however generating by-product hydrogen as result, which can then be reused in the sectors mentioned above improving the overall processes [66].

In terms of future prospects, hydrogen demand in the chemical industry is expected to increase from 44 Mt/year presently to 57 Mt/year by 2030, with ammonia rising 1.7% and methanol 3.6% from 2018 until 2030 [66]. It is worth noting however, that these percentages might even increase if both chemicals would be used as energy carriers in the future, thus broadening its application spectrum. In fact, ammonia is already being considered as an energy storage and transportation possibility, due to its technical properties which make such chemical less complex to implement compared to hydrogen [66].

**Steel production**

Iron and steel fabrication are both a heavy hydrogen consumer as well as a significant $CO_2$ pollutant industry. In fact, data provided by the World Steel Association in 2018 reported that about 1.85 tonnes of $CO_2$ were emitted per each ton of steel produced, which is equivalent to 8% of the total carbon emissions worldwide [68]. Furthermore, since steel demand is expected to rise 6% by 2030 [66], alternatives have to be considered regarding not only pollutant emissions, but also its hydrogen consumption, in particular for Direct Reduced Iron method for steel production.

Moreover, the conventional blast furnace basic oxygen furnace (BF-BOF) steel plant produces hydrogen as a by-product, which is a major component of the coke gas obtained from coal heating. Since not all this hydrogen is efficiently recovered and reused, further applications such as methanol production are already being considered. Assuming around 14 $MtH_2$/year are produced as a by-product, only 9 $MtH_2$/year are reused, while the remaining hydrogen is commercialized for other applications [66]. Such technology is responsible for 90% of the primary steel production [66], and has shown itself to be very hard to decarbonise, with current researchers studying the possibility to replace coal by hydrogen as the main reducing agent in the steel making process. Nevertheless, an alternative process for steel production, called direct reduction of iron-electric arc furnace (DRI-EAF) presents a promising decarbonisation pathway despite its small share of only 7% of the primary steel production worldwide. Such process uses a mixture of hydrogen and carbon monoxide as a reducing agent, meaning that green hydrogen from water electrolysis would be a key aspect to reach zero emissions goal [66],[68].

In order to DRI-EAF process to become cost competitive with the traditional existing blast furnace technologies, there are some important factors to analyse. Firstly, it has a huge dependency on the green hydrogen future cost, since it is a major component of the reducing agent mixture used. In addition, recent studies show that if up to 40% of recycled scrap metal would be used in the electric arc furnace process by 2030, clean steel would become an economical feasible solution in the market. In fact, direct reduction of iron-electric arc furnace could double its share in the primary steel demand, thus requiring around 8 Mt of $H_2$/year as a reducing agent [66].

**Green hydrogen for clean transport fuels**

Hydrogen represents a very interesting route regarding existing conventional transport fuels, and is expected to become a complementary alternative for battery electric vehicles. As already mentioned, hydrogen is a key gas for power-to-liquid applications, namely methanol, ammonia and synthetic methane, which ultimately are promising options for the diverse transport sectors.

For the road transport sector, existing electric vehicles are being considered as the most competitive option to reduce the current carbon emissions share from gasoline and diesel combustion, around 24% of the total global carbon emissions [68]. However, for the heavy-duty sector with inherent higher mileage ranges, such as trucks and buses, hydrogen fuel cells might be a good solution. In fact, hydrogen fuel cells as well as hydrogen internal combustion engines vehicles are expected to reach breakeven point with conventional diesel trucks by the year of 2030 [68]. In terms of the expenses related to hydrogen refuelling stations, there is still a long way to go through in order to achieve cost optimization. Current estimations show that $H_2$ refuelling infrastructures represent an investment between 0.12 and 1.7 million euros depending on the hydrogen required pressure, which can go from 350 to 700 bar [66]. It is no surprise that the compressor and the storage tanks have the highest percentages in the overall budget expenses for refuelling stations. Nevertheless, increasing its capacity from 50 to 500 $kgH_2$ per day would reduce the specific cost by 75% [66].

The maritime sector can also benefit from hydrogen as a shipping fuel to decrease carbon emissions, in order to reach the goal of the International Maritime Organization (IMO), to reduce sulphur and greenhouse gas emissions from shipping by at least 50% by 2050 (to 0.5 Gt of $CO_2e$) [68]. For short term solution, air pollution control devices are being used, as well as dual fuel engines, which operate with conventional heavy fuel oil and alternative fuels, such as liquified natural gas (LNG). As for the long run, other fuels are being considered such as, biofuels, synthetic methane, liquid clean hydrogen, green ammonia and green methanol [68].

Liquid clean hydrogen would require additional bunkering infrastructures, increasing its cost by 30% compared to LNG [66]. For this reason, other low emission alternatives might present themselves as more competitive solutions regarding long range maritime transportation. Nevertheless, for cruise ships, $LH_2$, together with green methanol, are feasible solutions, requiring about 250 €/tonne of $CO_2$ to breakeven with conventional fuel oil [68]. Container ships, however, might opt for green ammonia, since its toxicity levels would not be a factor due to the absence of passengers. Consultancy McKinsey & Company report that such fuel would reach breakeven with heavy oil at 85€ per tonne of $CO_2$ [68].

Lastly, the aviation sector, which perhaps currently faces the most complex challenges to be decarbonised due to physical and cost constraints, is responsible for the emission of 0.9 Gt of carbon dioxide annually (around 2% of the carbon emissions worldwide) [68]. With the IATA, International Aviation Transport Association aiming to reduce by 50% de $CO_2$ emissions by 2030, two distinct routes are presented as promising, hydrogen based liquid fuels (power-to-liquid technology) and liquid clean hydrogen, a less proven alternative and currently still in research and development phase [66].

Furthermore, the choice of one of these solutions will depend on the evolution of carbon prices, the aviation sector demand, the mileage range considered and naturally, government policy incentives. In fact, a recent study concluded that, for the case of synfuels, which leverage from operating in the existing jet fuel infrastructure, would require a carbon dioxide price between 95 and 548 € per tonne of $CO_2$ [66]. In addition, synthetic fuel is positioned as the most cost competitive long-term alternative for the case of long range flights, for a 10 000 km range and above [68].

Liquid hydrogen, in opposition, faces tremendous challenges for long range flights due to costly cryogenic storage requirements as well as infrastructure changes. For short to medium ranges, however, which are responsible for 70% of the total aviation carbon emissions [68], $LH_2$ surpasses power-to-liquid options regarding cost of available seat kilometre (CASK), considering a carbon price of around 75-125 €/tonne of $CO_2$ by the year of 2040 [68].

### 2.4.3 Green Hydrogen in Portugal

In this section, current and future hydrogen consumption is estimated for three major industries, namely oil refining, steel production and integrated combined cycle gas turbines.

The oil refining in Portugal is predominantly performed in two refineries owned by the Portuguese oil and gas company Galp, located in Matosinhos and Sines. Nevertheless, hydrogen consumption estimations will only be performed for Sines, since Matosinhos refinery is reported to close until the end of 2021. In fact, in 2014 Matosinhos refinery was reported to produce around 3 500 000 tonnes of refined crude, equivalent to 67% of its total refining capacity. Sines, the biggest refinery in Portugal reported a production of 8 600 000 tonnes of refined crude (around 68% of the plant´s total capacity) in the same year [69]. The following table exhibits the reported quantities of the obtained refined products from crude oil for the case of Matosinhos and Sines in 2014.

Table 5 – Quantity of refined products from crude oil (in tonnes) in 2014 (Adapted [69])

| Product | Matosinhos | Sines |
|---|---|---|
| Diesel | 1 552 664 | 3 645 197 |
| Gasoline | 230 854 | 1 680 608 |
| Fuel oil | 718 122 | 1 538 463 |
| Jet fuel | 718 122 | 891 545 |
| LPG | 53 799 | 225 922 |
| Others | 858 904 | 598 931 |

Assuming an average consumption of 10 kg of $H_2$ per tonne of refined crude oil [66], an annual demand of 86 000 tonnes of $H_2$ can be estimated for the case of Sines refinery.

For the steel industry in Portugal, some assumptions were made, based on literature review. It was considered that 1809 million tonnes of steel are produced annually and that Direct Reduced Iron will consume around 8 million tonnes of $H_2$ per year by 2030, with an expected share of 14% of the total primary steel demand in the world [66]. Thus, assuming an average value of 140 thousand tonnes of steel produced annually in Portugal [39], a demand of 4422 tonnes of $H_2$ was estimated, for the case of DRI electric arc furnace.

Ultimately, the possibility of blending hydrogen with natural gas in the gas turbines of combined cycle powerplants was analysed. In fact, recent studies show that between 3 a 5% of hydrogen can be used by current gas turbines without significant changes in their operation design [66].

Table 6 exhibits the current natural gas combined cycle powerplants in operation in Portugal, as well as their future hydrogen demand, considering 5% $H_2$ blend in the gas turbines [66]. The total natural gas consumption by the thermal power stations in the Portuguese energy system registered a daily maximum value around 136.5 GWh in the 16$^{th}$ of October 2020, which represents an increase of around 1.5% compared to the previous daily record, registered in the 17$^{th}$ of August 2017 [70]. Furthermore, according to data provided by the Portuguese Energy and Geology Institute, combined cycle powerplants consumed around 131 471 TJ (36 523 GWh) of natural gas in 2020 [71].

Table 6 – Combined Cycle Powerplants in Portugal and future hydrogen demand (Adapted [43], [66],[71])

| Combined Cycle Powerplant | Location | Installed Power Capacity (MW) | Electricity production percentage (%) | Natural Gas consumption (GWh) | Future $H_2$ consumption (tonnes) |
|---|---|---|---|---|---|
| Tapada do Outeiro | Gondomar | 990 | 25,9% | 9443,0 | 14052,2 |
| Lares | Figueira da Foz | 826 | 21,6% | 7878,7 | 11724,4 |
| Pego C.C. | Abrantes | 837 | 21,9% | 7983,7 | 11880,5 |
| Ribatejo | Alenquer | 1176 | 30,7% | 11217,2 | 16692,3 |
| **Total** | - | 3829 | 100,0% | 36522,6 | 54349,3 |

In conclusion, integrated combined cycle power plants in Portugal will be a considerable green hydrogen consumer with a total estimation demand of 54 349.3 tonnes per year of hydrogen, considering all 4 existing power stations. In fact, a special emphasis is given to Ribatejo's power plant, with a 1176 MW installed capacity and a future $H_2$ demand of 16 692.3 tonnes. Moreover, as improvements are made regarding hydrogen blending with natural gas, cost effective retrofitting can be performed in the gas turbines in order to maximize the hydrogen percentage in the fuel gas mixture. For an optimistic case scenario, where gas turbines would operate with 100% hydrogen instead of natural gas, significant changes would have to be addressed in the entire operation design of such infrastructure, which ultimately represent an intensive capital investment.

# 3 Results and Discussion

## 3.1 Geographical Assessment

In this section, a thorough analysis is made with the aim of identifying the regions of Portugal where the highest oxygen and hydrogen consumers are located. In order to do so, the Excel tool 3D Maps was used, where several layers were added.

Firstly, this study starts to identify possible existing renewable energy technologies in Portugal which could be used to power the electrolysers, namely wind and solar PV. As it can be seen in figure 36, wind energy is mostly located in the northern region, whereas figure 37 shows that solar has a higher installed capacity in the Southern region, due to larger solar irradiance characteristics. Furthermore, wind energy in Portugal has a total installed capacity of 5,449.38 MW (39.2%), with the highest power capacity districts being Viseu (1,130.40 MW), Coimbra (752.01 MW) and Vila Real (681.10 MW) [72].

On the other hand, the total solar installed capacity in Portugal is 492.79 MW (3.5%), with increased presence in the districts of Beja (165.36 MW), Évora (77.18 MW) and Setúbal (67.51 MW) [72].

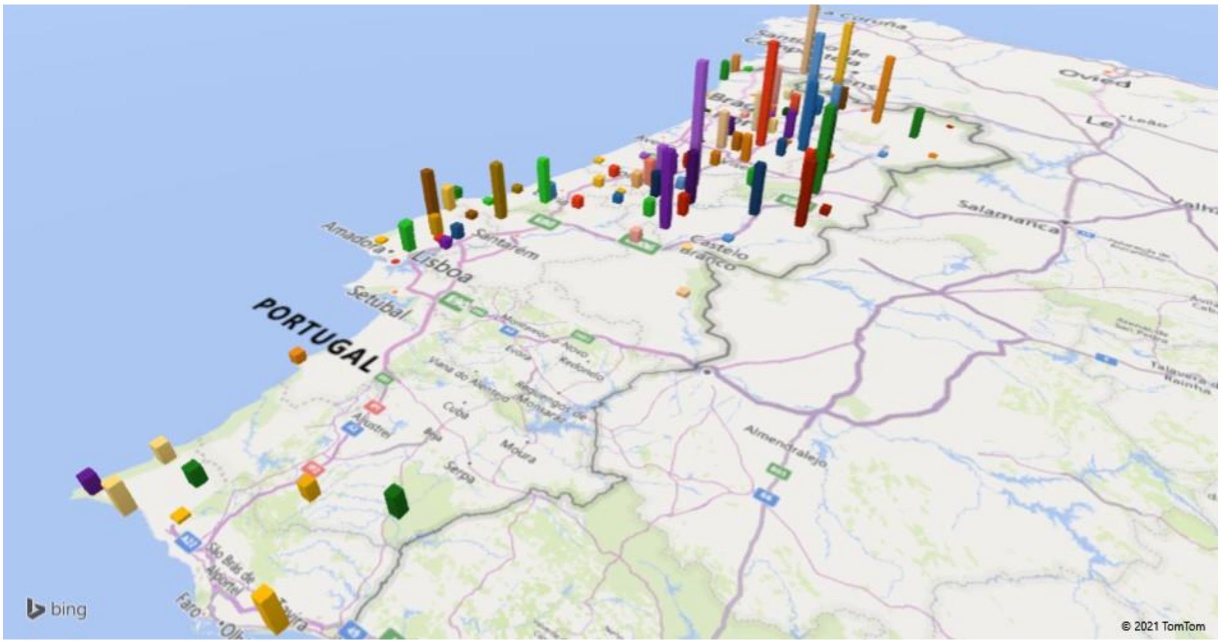


Figure 36 - Wind Installed capacity in Portugal (MW)


Figure 37 – Solar PV installed capacity in Portugal (MW)

The caption of both figures 36 and 37 can be found in the Appendix A, with the respective installed capacity by Portuguese district and municipality. Also, even though solar and wind installed capacity in the Archipelagos of Madeira and Azores are not shown in the maps above, such renewable energy presence should not be neglected. In fact, Madeira has 11.2 MW solar and 46.2 MW wind installed capacity. On the other hand, Azores only has 1 MW solar and 36.65 MW installed wind capacity.

For the pulp bleaching layer, 6 major locations in Portugal were identified as high industrial oxygen consumers (figure 38). Three companies were considered for the paper industry analysis, namely Altri [47] (which owns the companies Celtejo, Caima and Celbi), Navigator [46], and DS Smith [48]. In fact, as already mentioned earlier in this study, Figueira da Foz has tremendous interest as an industrial oxygen consumer, with an estimation value demand of 61 650 tonnes of $O_2$ per year, followed by Navigator´s factory in Setúbal which is estimated to consume 24 750 tonnes of $O_2$/year. Note, however, that such calculations were based in the maximum annual production capacity reported by each pulp factory, and not the actual quantity of pulp produced. In fact, previous calculations performed in the industrial oxygen comparative section of this study, assumed a total oxygen demand in Portugal for the pulp industry of around 72 000 tonnes of $O_2$ /year, considering a total amount of 1.6 million tonnes of paper produced in 2019 [38] and an average demand of 45 kg $O_2$/tonne of pulp [28]. Thus, considering that the total paper production capacity requires around 125 100 tonnes $O_2$/year, it can be concluded that in 2019, the paper industry in Portugal operated at 57.6% of its maximum capacity.


Figure 38 – Pulp Bleaching Oxygen consumption in Portugal (tonnes/year)

Iron and steel production are both an oxygen and hydrogen consumer, thus being a very interesting sector. As already mentioned, Steel traditional blast furnace in Portugal was estimated to consume around 22 500 tonnes $O_2$/year, assuming an oxygen demand of 162 kg $O_2$ per tonne of steel produced [26]. As for the hydrogen consumption, an average consumption value of 32 kg of $H_2$ per tonne of steel produced was assumed, considering Direct reduced iron process [66]. Thus, considering 140 thousand tonnes of steel being produced annually in Portugal [39], a total demand of 4422 tonnes of hydrogen per year can be estimated for the Portuguese steel industry. Interestingly, the steel industry requires 5 times more oxygen than hydrogen, assuming the conventional process of blast furnace. As government pressure to reduce the carbon emissions in the steel sector rises, many facilities will change to OBF processes, which in such case would consume almost 14 times more oxygen than hydrogen [26].

Moreover, there are essentially 3 major foundries in Portugal, 2 located near Porto and 1 in Lisbon [73]. Due to lack of information regarding the annual steel production in each plant, all three foundries were assumed to have equal annual production capacity, as shown in figure 39.

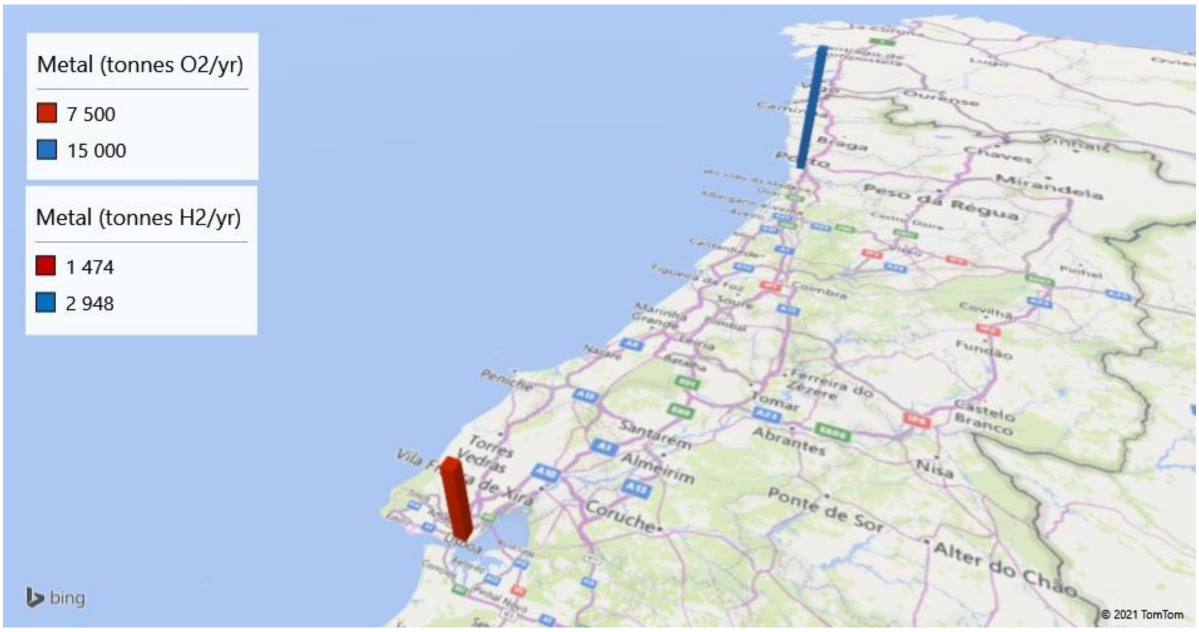


Figure 39 – Oxygen consumption for the Steel industry in Portugal (tonnes/year)

The glass industry has proven to be the most promising industrial oxygen consumer in Portugal, due to the quantity of glass produced annually, reported to be 1.5 million tonnes annually [40]. As previously estimated earlier in this paper, 600 thousand tonnes of oxygen per year were assumed for the Portuguese glass industry considering glass oxygen combustion furnace. In addition, the 6 main Portuguese glass factories are located in Vila Nova de Gaia (1 plant), Figueira da Foz (1 plant), Amadora (1 plant) and Marinha Grande (3 plants) [40]. Once again, all factories were estimated to have equal annual glass production capacity, shown below in figure 40.

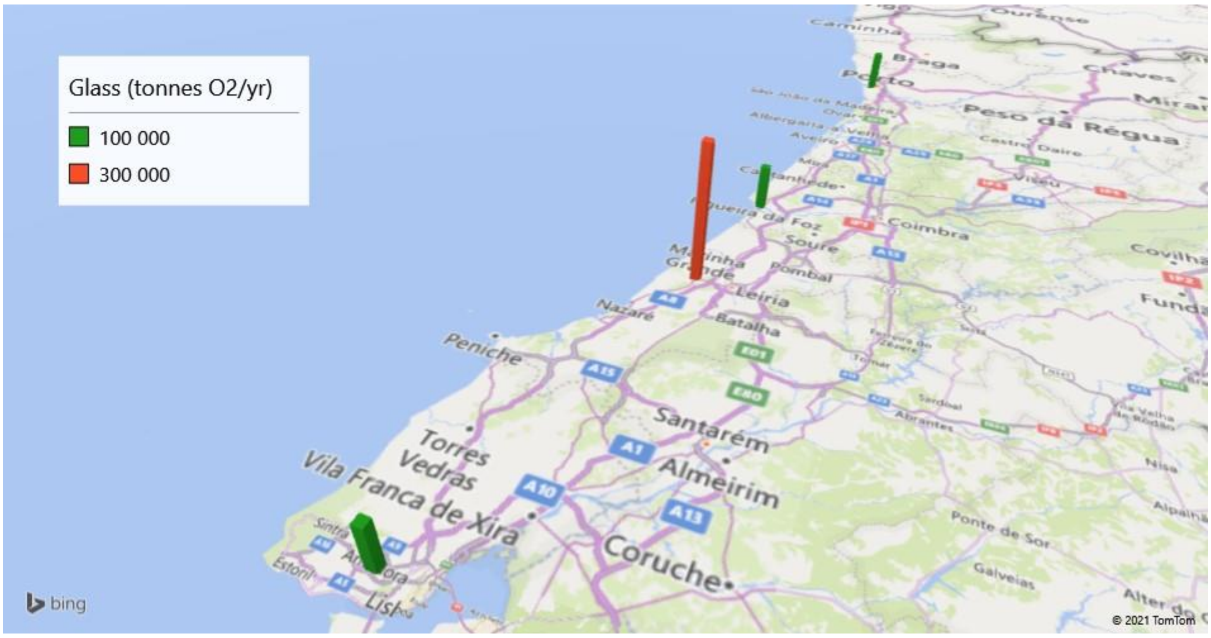


Figure 40 - Glass industry Oxygen consumption in Portugal (tonnes/year)

For the wastewater treatment sector, in order to estimate the oxygen demand in each Portuguese region, a correlation was performed based on the territory population density. In fact, Portugal was reported to have 111.5 habitants/km$^2$ in 2019 [74]. For the present scenario, the 20 most populated municipalities were considered. Sines was also included due to the promising future project announced by the Portuguese government, regarding the instalment of electrolysers for green hydrogen production and exportation [51]. Thus, assuming a total oxygen demand of around 28 044 tonnes of $O_2$ annually for sludge treatment processes [28], [41], an estimation value of 1.78 tonnes of $O_2$/year per habitant/km$^2$ can be assumed for calculation purposes. The 3D Map below exhibits the geographic assessment of these particular locations mentioned.

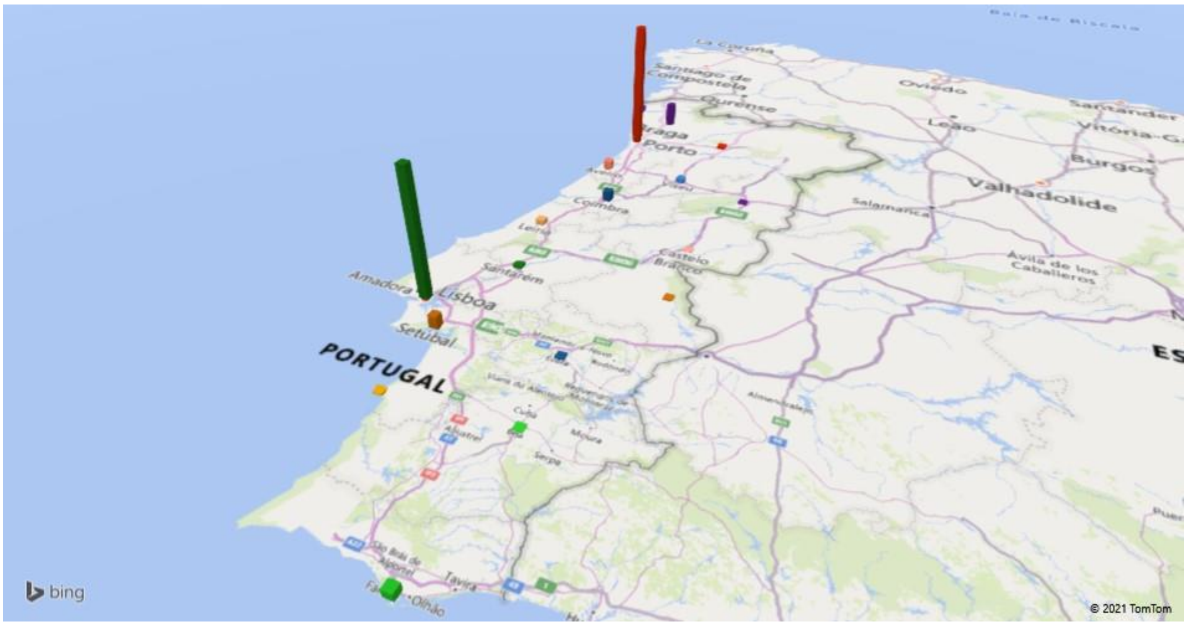


Figure 41 – Wastewater treatment oxygen consumption in Portugal (tonnes/year)

As it can be seen, Lisbon (9044 tonnes/year), Porto (9280 tonnes/year) and Braga (1769 tonnes/year) show the highest oxygen demand for the wastewater treatment sector, since these are the districts with the highest reported population density. Nevertheless, it is important to mention that such correlation used is not entirely accurate, considering that the significant water pollutants are industrial sites and not exactly the population itself. The estimated oxygen consumption values for the other Portuguese regions, archipelagos included, can be found in Appendix A.

Furthermore, for the layer regarding medical oxygen consumption, a representative sample was chosen to study the location of the hospitals with the highest, average and lowest annual oxygen demand (Appendix A), as has been previously shown in figures 30, 31 and 32.

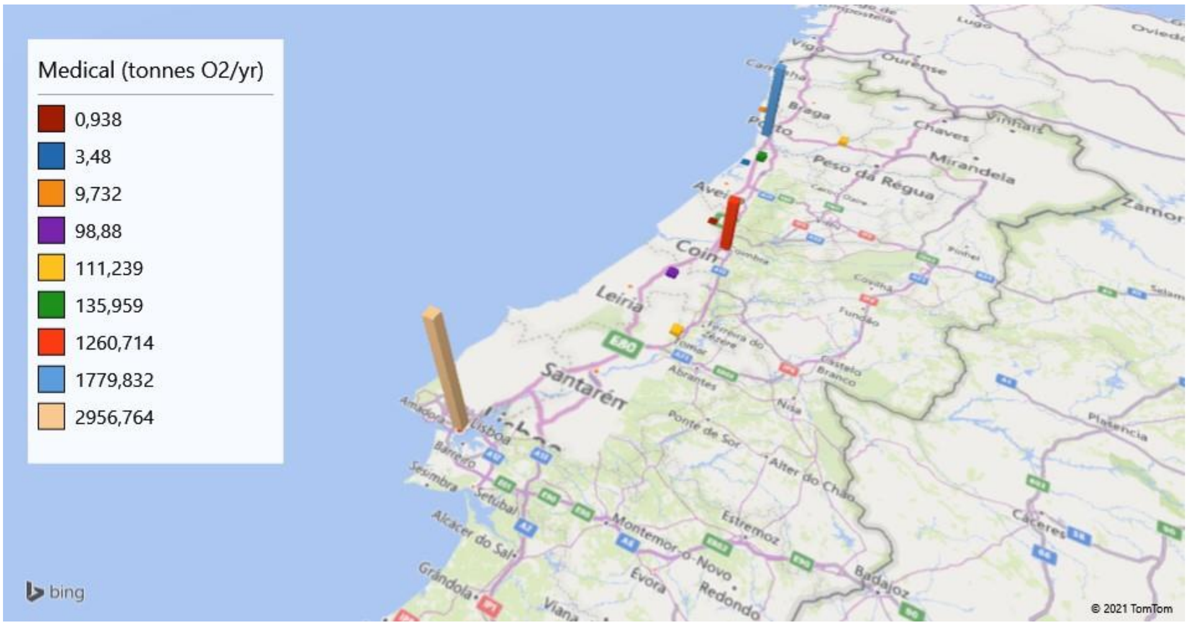


Figure 42 – Medical use Oxygen consumption in Portugal (tonnes/year)

As it can be seen from the 3D Map above, the regions with the highest medical oxygen demand are Lisbon (2957 tonnes of $O_2$/year), Porto (1780 tonnes of $O_2$/year) and Coimbra (1261 tonnes of $O_2$/year). It is important to underline that, as already shown in the previous section of this study, home caring medical oxygen plays an equally important role in the hospital gases market. The major economic added value derives from its transportation and storage, being delivered via costly cylinders, instead of via regular bulk liquid oxygen, which is the case of most hospitals and healthcare centres.

The crude refining sector was also characterized geographically, since it has proven to be the biggest industrial hydrogen consumer. The only oil refining plant in Portugal is located in Sines, with an annual demand of around 86 000 tonnes of $H_2$ for hydrotreatment and hydrocracking treatments [66], [69].

In addition to the oil refining sector, the 3D map below shows the location of the 4 natural gas combined cycle power plants in Portugal, whose technical characteristics and future hydrogen consumption were shown in table 6, in the previous section of this paper.


Figure 43 – Oil refining and Combined Cycle Gas Turbines (CCGT) annual hydrogen consumption (tonnes/year)

Finally, all the 8 layers above were overlaid, according to geographical location as well as the weight of each industrial sector in Portugal. For instance, the Oil refining sector, being the industry with the largest grey hydrogen consumption, was assumed to have a weight of 45%. In fact, green hydrogen electrolysers near oil refineries are crucial to decarbonize such a heavy pollutant sector in the near future. As for the oxygen consumers, the medical sector and the glass industry in Portugal were assumed to also represent significantly weight (20% and 10% respectively), due to the large medical oxygen market price and the fact of glass industry being the largest industrial oxygen consumer. All other layers represent 5% weight each, as shown in table 7.

Table 7 - Average weight of each layer in the Portuguese Industry

| **Layer** | **Weight (%)** |
|---|---|
| Pulp Bleaching (tonnes O2/year) | 5 |
| Glass (tonnes O2/year) | 10 |
| Medical Oxygen (tonnes O2/year) | 20 |
| Wastewater Treatment (tonnes O2/year) | 5 |
| Metal (tonnes O2/year) | 5 |
| Metal (tonnes H2/year) | 5 |
| Oil Refinery (tonnes H2/year) | 45 |
| CCGT (tonnes H2/year) | 5 |
| **Total** | 100 |


Figure 44 - Final geographical assessment for electrolysers installation in Portugal

As it can be seen from figure 44, Sines has the highest potential, not only due to geographical factors (namely proximity to a seaport and high solar radiancy levels) but also due to the refining sector importance. Other promising areas are Lisbon (biggest medical oxygen consumer in Portugal) as well as Marinha Grande (largest glass industry location), Figueira da Foz (paper industry sector and combined cycle powerplant), and Porto (second largest medical oxygen consumer and strong steel industry for the oxygen consumption).

## 3.2 Economic Analysis

### 3.2.1 General Considerations

A sensitive analysis was performed for the installation of a 1 MW Alkaline Electrolyser, powered by solar electricity (1.25 MW peak power PV Plant). In fact, Alkaline technology was considered for representing the lowest Capex amongst available options, of 900 €/kW [75]. Solar energy is currently the most cost effective renewable source in Portugal, having reached in 2020 a historic price around 11 €/MWh [76].

Different scenarios were analysing, considering a proprietary PV plant and the case where both the electrolyser and the solar PV have to be purchased. In fact, the latter case is likely to be the most common option, since none of the preferred locations in Portugal assessed above have enough installed solar capacity currently. In addition, it is noteworthy to evaluate the land availability, since a 1.25 MW solar PV plant is expected to occupy around 0.6 to 0.8 ha [77]. Furthermore, this study underlines the impact of selling oxygen in the financial model evaluation of the plant. According to calculations, industrial oxygen was assumed to represent 87% of the Portuguese market share at an average price of 0.15 €/kg, whereas medical oxygen (homecare treatment included) represented only 13% market share at a selling price of 4.3 €/kg. Thus, an average value of 0.7 €/kg of $O_2$ was chosen to be a representative value for by-product oxygen selling. Hydrogen selling price was assumed at 10 €/kg to reach economic feasibility. A key insight from these calculations is the weight of both $H_2$ and $O_2$ compression and storage costs in the financial model. Distribution costs were neglected in the analysis, since the aim of this project is to install the electrolyser near the final consumers. In fact, in a highly optimistic future scenario, compression and storage costs could also be largely reduced or even neglected. Sectors like the paper industry, steel, glass and even ceramics, which are heavy oxygen consumers could truly benefit from this, only having the electrolyser operating during the factory production hours, thus consuming oxygen (and for the steel industry both $H_2$ and $O_2$) in real time via a direct line with no further costs associated. For this case, calculations were obtained with hydrogen selling price at 8 €/kg. However, note that currently the majority of hydrogen is still obtained by Methane Steam Reforming, where current $H_2$ market price is around 2 €/kg[75]. Therefore, in order for green hydrogen to be competitive with current grey hydrogen production, its market price have still a long way to go until both technologies are available at similar cost. Clearly, government funds and tax redemption (due to avoidance of $CO_2$ emissions) are crucial. In addition, there are other components which have a powerful contribute to the final cost of green hydrogen, related to the electrolyzing process itself. The main parameters with the higher influence are the electrolyser full load capacity, the renewable source electricity price and some key components in the Capex of the final system, namely the electrolyser cost as well as the compression and storage system required for both gases (hydrogen and oxygen).

The 1 MW alkaline electrolyser considered, with 70% efficiency is able to produce 41580 kg $H_2$/year and 331800 kg $O_2$/year, considering 2100 hours in operation annually [75]. In order for a country like Portugal truly benefit from such investment, capacity scale-up is essential once technology maturity is obtained and the electrolyser costs decrease. In fact, for the existing oil refining in Sines, which consumes 86 000 tonnes of $H_2$ annually, approximately 2 GW of installed Alkaline electrolysers would be required just to cover internal consumption. If Sines would want to benefit from its location and further export hydrogen to central Europe, a larger installed capacity is imperative. For the example of medical oxygen consumption in Portugal, a 9 MW electrolysis system would have to be installed in Lisbon to cover the annual demand. In fact, the 1 MW reference base used in this study would only cover medical oxygen expenses for 3990 hospital beds, according to the correlation previously shown (figure 34).

### 3.2.2 Mathematical approach

The mathematical approach used in this study was based on literature review [78], [79] with the final aim of assessing different metrics such as the Capital expenditures and Operational costs involved in building such plant, the levelized cost of Hydrogen, NPV, Payback period and IRR.

The net present value can be characterized as the current value of all the future cash flows generated during the plant´s lifetime, which was assumed to be 20 years. Therefore, it can be calculated using the following expression, being $N$ the number of periods, $CF_n$ the cash flows at time $n$, $r$ the discount rate and $I_0$ the initial investment:

$$NPV = \sum_{n=1}^{N} \frac{CF_n}{(1+r)^n} - I_0 \quad (7)$$

As for the Levelized Cost of Hydrogen (LCH) some modifications were made, in order to include by-product oxygen sales as a revenue increment (respecting the relation of 8 kg of $O_2$ for each kg of $H_2$ produced).

Moreover, the formula used does not take into account compression and storage costs, in order to maximise the potential of using a direct line from the electrolyser plant to the local consumers. The expression used is given below, and depends on some main technical parameters such as the solar electricity cost, the electrolyser capex, the plant lifespan, the total operating hours, the specific consumption and the electrolyser's efficiency:

$$LCH(€/kg) = \left(\frac{ELCTR(\frac{€}{MWh})}{1000} + \frac{CAPEX\ (\frac{€}{kW})}{20\ Years} \times \frac{1}{FLH(h/Year)}\right) . \frac{Specific\ Consumption(\frac{kWh}{kg})}{Efficiency} - Revenue\ \ O_2(€/kg)\ \times 8\ \times\ \%O_2\text{sold} \quad (8)$$

The Internal Rate of Return (IRR) was also evaluated. It represents the discount rate for which the NPV of an investment is zero. In fact, a project with good evaluation has an IRR superior than the discount rate, which for the present case, was assumed equal to 5%. Thus, IRR can be given by the equation below:

$$\sum_{n=0}^{N} \frac{CF_n}{(1+IRR)^n} = 0 \quad (9)$$

The payback period was obtained by dividing the initial investment cost of a project by the amount of net cash inflow that the project generates each year. For simplification purposes, the net cash inflow was assumed to be constant each year.

### 3.2.3 CAPEX and OPEX estimation

All parameters used for the economic assessment are presented in the tables below (8 to 12). Table 8 shows the financial and tax parameters considered. Note that no inflation rate is currently used by the Portuguese banks. Besides, an interesting input in this study is a suggested tax redemption, to be implemented by the local governments. In fact, such assumption makes total sense, in order to rapidly scale up green hydrogen into the market, while reducing carbon emissions associated to steam methane reforming. Such technology, which is still the main process used to produce grey hydrogen, produces around 7 kg of $CO_2$/kg of $H_2$ [80]. Carbon taxes price have been increasing drastically over the years. In fact, Europe has already surpassed the barrier of 50 €/tonne of $CO_2$ [81] and experts are confident that such price will continue to rise. For the purpose of this study, a tax redemption is proposed, which represents the amount of $CO_2$ saved annually by producing hydrogen using a 1MW electrolyser, considering a reference carbon tax price of 60 €/tonne of $CO_2$.

Table 8 - Financial and tax Parameters

| Parameter | Value | Ref. |
|---|---|---|
| Equity rate of return | 5% | |
| Inflation rate | None | |
| Tax rate on earnings | 15% | |
| Tax redemption ($CO_2$ emissions) €/year | 17464 | [80], [81] |

Table 9 shows the main parameters of the plant, such as the expected plant lifetime (20 years), the stack lifetime (83 000 h), the full load hours (assuming 6h/day plant operation), and both gases output. Besides, the actual specific energy consumption is about 47.6 kWh/kg of $H_2$, considering 70% efficiency from the alkaline electrolyser (the given theoretical energy consumption is 33.3 kWh/kg) [75].

Table 9 - Plant Characteristics

| Parameter | Value | Ref. |
|---|---|---|
| Electrolyser power | 1 MW | |
| PV plant peak power | 1.25 MW | |
| Total Power Generated by PV plant | 1625000 kWh/yr | [77] |
| Electrolyser efficiency | 70% | [75] |
| Plant lifetime | 20 years | [77] |
| Stack lifetime | 83 000h | [77] |
| Full Load Hours (h/year) | 2100 | [75] |
| Theoretical energy consumption | 47.6 kWh/kg $H_2$ | [75] |
| Hydrogen output (kg/year) | 41580 | |
| Oxygen output (kg/year) | 331800 | |

Table 10 - Alkaline water electrolysis plant costs

| Investment | Cost | Ref. |
|---|---|---|
| 1MW Electrolyser | 900€/kW | [75] |
| Solar electricity cost | 11 €/MWh | [76] |
| Compression plant ($H_2$ and $O_2$) | 1 500 000 € | [77] |
| Storage system | 115 278 € | [78] |
| 1.25 MW Solar PV installment cost | 700€/kW | [77] |
| Total direct depreciable capital cost (ddcc) | 2 872 778 € | |
| Indirect depreciable capital cost (idcc) | 20% | [77] |
| Fixed O&M costs: | | |
| Material | 2.5%/ddcc | [77] |
| Labour | 5%/ddcc | [77] |
| Variable costs: | | |
| see table 11 | | |

Table 10 exhibits the main parameters regarding the Capex and Opex of the electrolysis plant. In fact, Capex includes the 1MW electrolyser cost, storage and compression costs and also solar electricity cost. The cost of a standard hydrogen compression system (200 bars) alone was derived from literature review and assumed to represent around 1 000 000 € [77]. Oxygen, since it occupies half the volume of hydrogen when compressed at the same pressure of 200 bars, its compression plant was estimated to represent half the investment, around 500 000 €. Other compression alternatives are available in the market, namely by varying the electrolyser´s operating pressure or via a separate electrochemical device [82]. However, these alternatives are still premature, since an added cost had to be considered in the electrolyser design, or, for the case of the membrane, permeability issues would be encountered. This parameter is the most capital intensive in the overall plant. However, plant scale up and early offtake agreements with interested industries can reduce the compression and storage costs. Operational expenses are divided in fix and variable costs (table 11). Fixed operational costs include material (2.5% ddcc) and labour (5%/ddcc) based on literature review. Note, however, that these percentages are expected to decrease with the scale up of the plant capacity. As for the variable costs, shown in table 11, there are some costs related to the use of some upstream products that are required for the alkaline water electrolyser operation. The main variable cost is from water impurities removal (deionised water), which has the largest specific demand (around 9 kg/kg of $H_2$). Nevertheless, according to the International Renewable Energy Agency, the ionized water and cooling systems can decrease its specific cost by 60% when increasing the manufacturing scale of the electrolyser plant [82]. In addition, other products are required, namely a potassium hydroxide solution, whose purpose is to avoid corrosion issues during the process. Typically, such KOH solution should be changed after a period of 10 years of operation. During this operation time, the KOH solution is recirculated without requiring any kind of conditioning [83]. For this reason, for calculation purposes, KOH operational cost was only considered in the first year and in year 10. Lastly, steam is used to heat up the system, as well as nitrogen for gas cleaning purposes.

Table 11 - Upstream products

| Product | Specific demand | Cost | Ref. |
|---|---|---|---|
| Deionised water | 8.9 kg/kg H2 | 0.004 €/kg | [79], [82] |
| KOH | 0.275 g/kg H2 | 2.5106 €/kg | [79], [83] |
| Steam | 0.038 kg/kgH2 | 0.01€/kg | [79], [83] |
| Nitrogen | 0.07115 g/kg H2 | 0.2783 €/kg | [79], [83] |

Finally, Table 12 represents the capital cost of a 1.25 MW solar PV plant, for the case in which the PV has also to be purchased. Once again, fixed operational costs include material and labour costs, also represented as a percentage of the direct depreciable capital cost, for simplification purposes.

Table 12 - PV Plant costs

| Investment | Cost | Ref. |
|---|---|---|
| Direct depreciable capital cost (ddcc) | 875 000 € | [77] |
| Indirect depreciable capital cost (idcc) | 5%/ddcc | |
| Fixed O&M costs: | | |
| Material | 2.5%/ddcc | [78] |
| Labour | 2.5%/ddcc | [78] |
| Variable O&M costs: | | |
| none | | |

A comparison was made regarding the costs and revenues for the two cases considered, the first including compression and storage costs (where $H_2$ is sold at 10 €/kg) and the second case, which is based on a direct line and real time gases consumption (where $H_2$ can be sold at 8 €/kg).

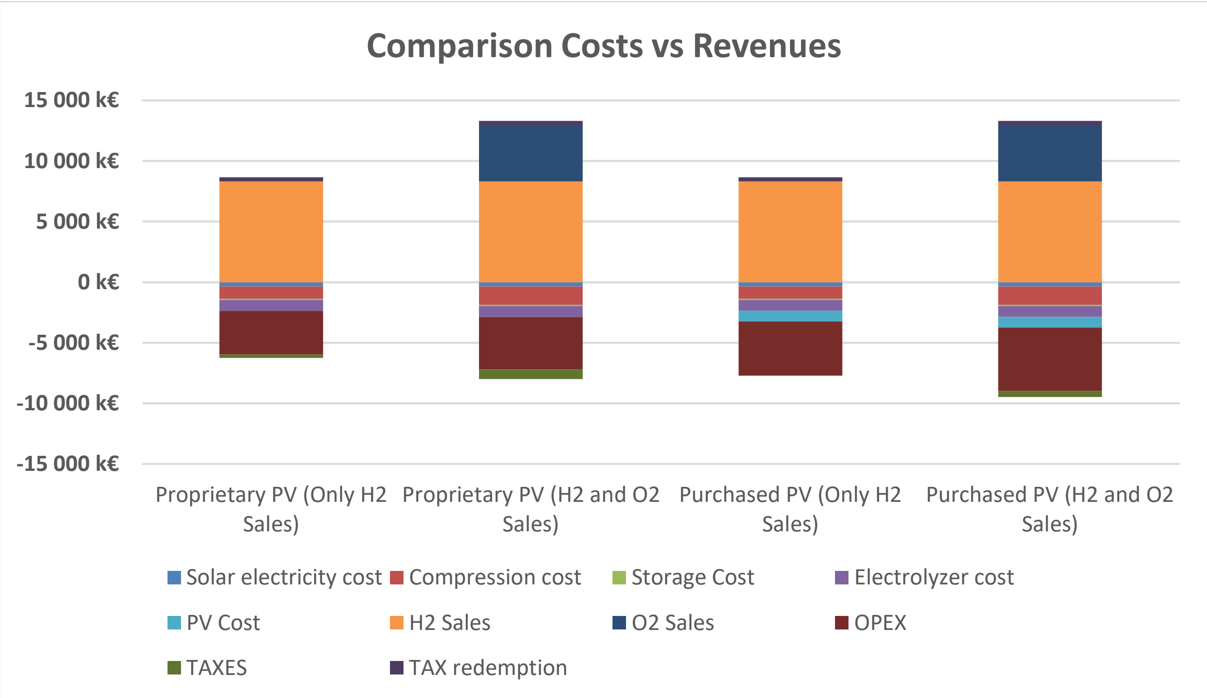


Figure 45 - Costs vs Revenues for several scenarios (considering $H_2$ selling price 10€/kg)

It is clear from Figure 45 that the main cost parameters are from the compression plant and the electrolyser, followed by the PV instalment cost. Total revenues include constant sales of both hydrogen and oxygen throughout the 20 years plant lifetime, as well as the proposed tax redemption. $H_2$ revenues account for 8 316 000 €, while oxygen sales represent a revenue of 4 645 200 €. As for the tax redemption, a total value of 349 272€ is proposed for the complete project. Even though the final residual value of the plant is not taken into account in these calculations, such parameter should be included in future work. Since there are few electrolysers currently operating, and none of them has reached end life, it is quite difficult to estimate such salvage value. However, typical compression and storage systems have longer lifetimes than the electrolyser itself, which would add economic value during decommissioning.

Figure 46 shows the share of each parameter for a more optimistic scenario, where gases are provided via direct line, thus compression and storage costs are neglected. Such avoidance translates into a very interesting financial outcome, since these two parameters were assumed to represent around 43% of the total CAPEX (considering that both the electrolyser and the PV plant had to be purchased).

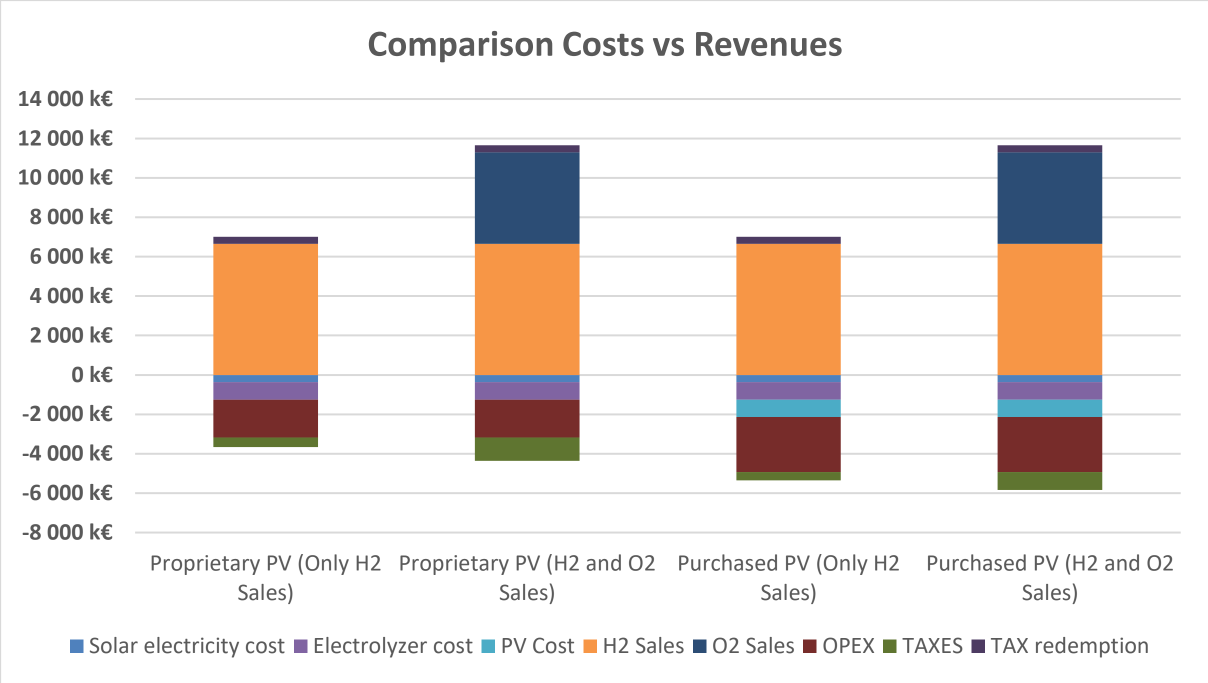


Figure 46 - Costs vs Revenues for several scenarios considering real time gases consumption ($H_2$ selling price 8€/kg)

### 3.2.4 Green Hydrogen Cost

The chart below exhibits the evolution of the $H_2$ cost over the years, based on the LCH formula used (equation 8), which neglects the compression and storage costs. In fact, it worth noting the profitability of selling the co-produced oxygen for this case, where both gases are consumed in real time. In fact, by supplying $H_2$ and $O_2$ via a direct line, not only it is possible to avoid unnecessary costs, but also to avoid electricity usage when the nearby industry consumers are not in operation. For instance, by 2030, $H_2$ cost considering 100% of oxygen sold would cost around -4€, meaning it would actually be a lucrative business. For the case where no oxygen was to be sold, green hydrogen would still be cost competitive in relation to grey hydrogen, around 2€/kg.

As for the solar electricity cost forecast, historic values were extracted from the international renewable energy agency IRENA [84]. Solar costs suffered a significant drop from 2010 to 2020, and are expected to remain stable around 10 to 12 €/MWh.

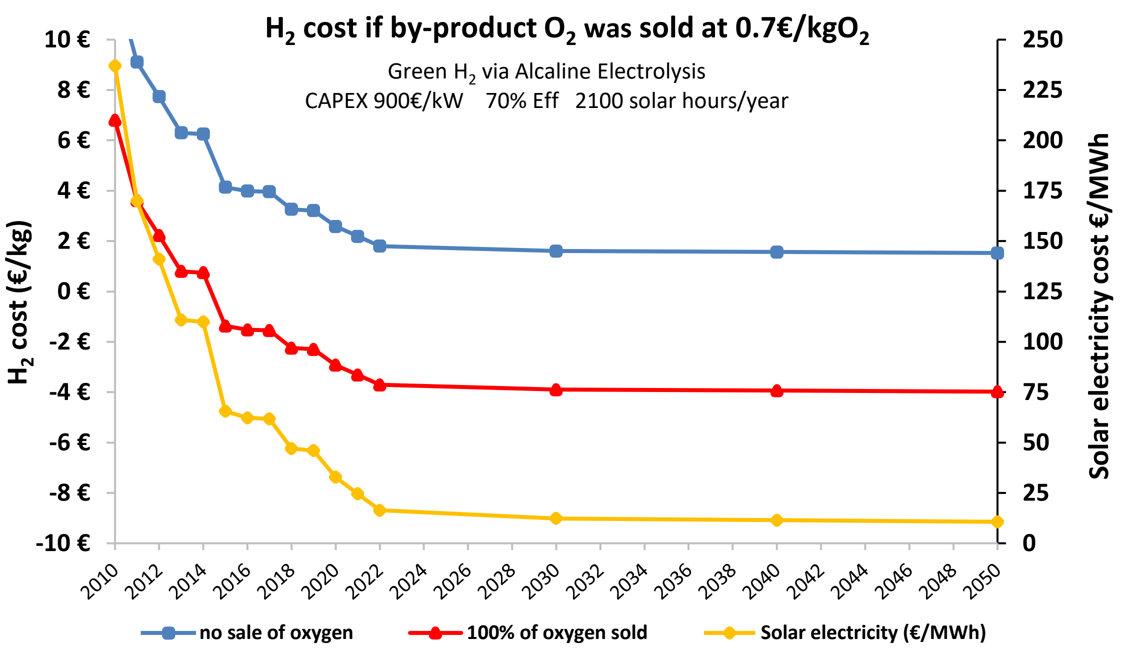


Figure 47 - $H_2$ cost (€/kg) and Solar electricity cost (€/MWh) forecast [84]

### 3.2.5 NPV

Figure 48 and 49 exhibit the NPV calculated for all different cases, as well as the impact of having a direct line for hydrogen and oxygen from the plant to the final consumer. In fact, it can be seen that the NPV value of the project for the scenario where gases are consumed in real time is much higher than for the case where compression and storage costs are considered. In addition, only for the case when the owner sells $H_2$ alone (and has to purchase the PV plant) the NPV is negative, for both scenarios studied.

For the most optimistic case, where the owner already has the PV plant installed and aims to sell both gases, the NPV is 2.3 times higher considering real time gases consumption, in comparison to the previous conservative scenario. If the PV has yet to be purchased, but the owner still intends to sell both gases, the NPV is 7 times larger if gases are delivered via direct line. Such results clearly underline the impact of selling oxygen in the final economics of the project as well as the tremendous potential of a direct line to be used, showing this can be a very attractive business.

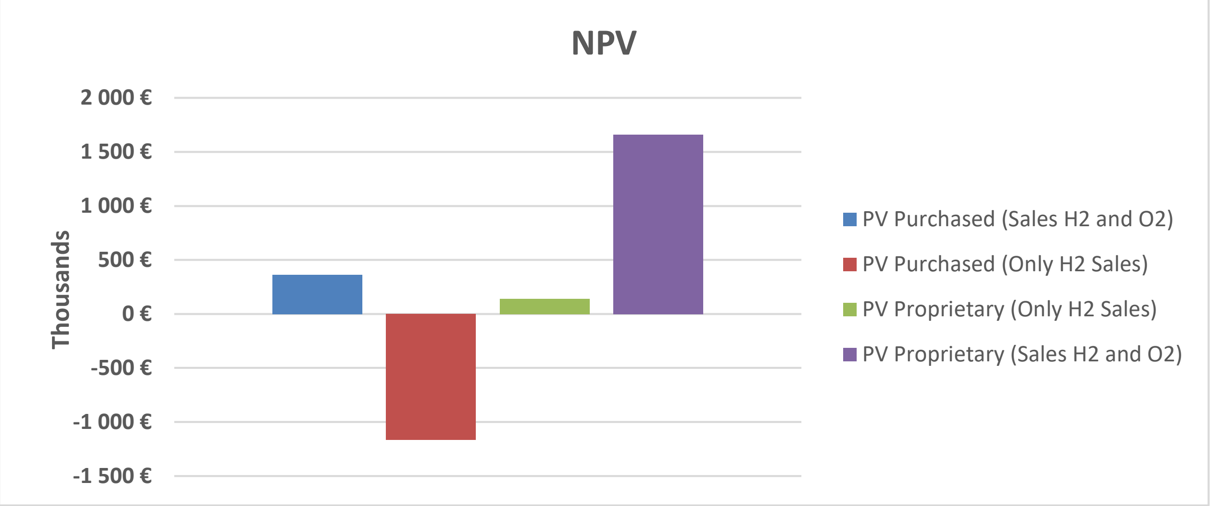


Figure 48 - NPV for several scenarios (considering $H_2$ selling price 10 €/kg)

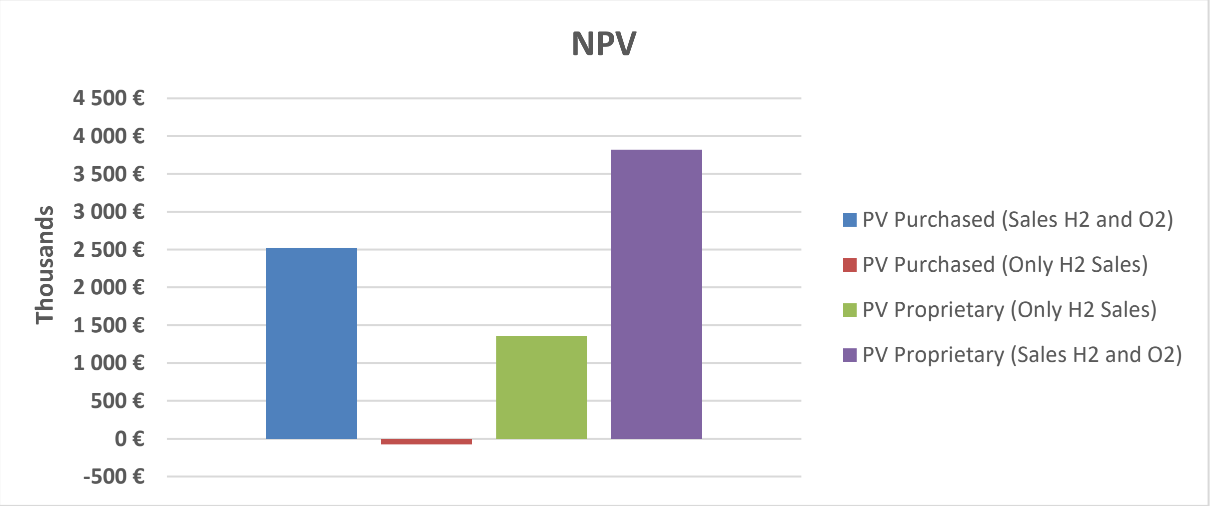


Figure 49 - NPV for several scenarios considering real time gases consumption ($H_2$ selling price 8 €/kg)

### 3.2.6 IRR and Payback Period

The internal rate of return and the respective payback period of all cases is represented in figures 50 and 51.

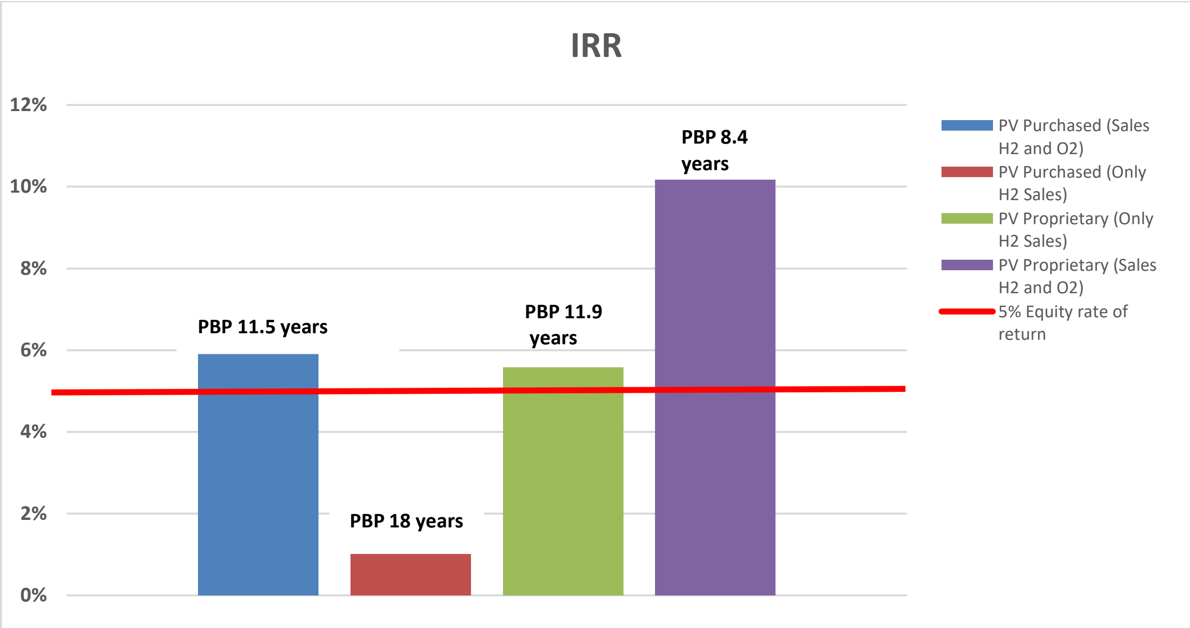


Figure 50 - IRR for several scenarios (considering $H_2$ selling price 10 €/kg)

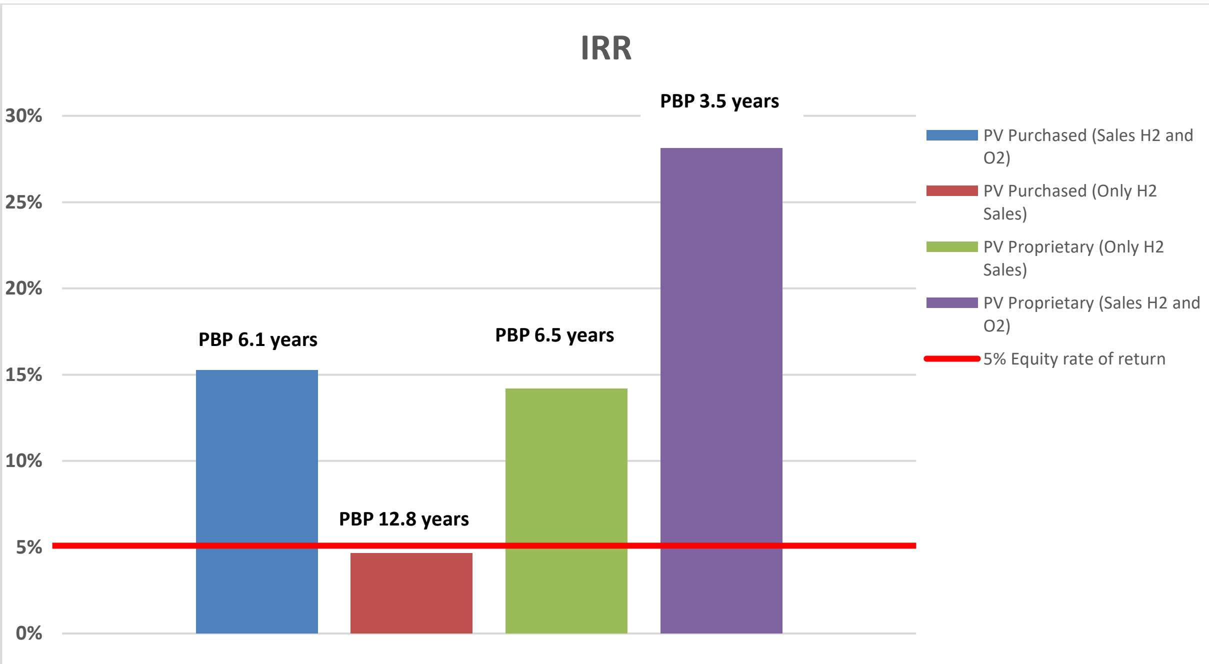


Figure 51 - IRR for several scenarios considering real time gases consumption ($H_2$ selling price 8 €/kg)

From figure 50 it can be seen that the IRR obtained is superior than the equity rate of return considered of 5% for all cases except for the one in which the PV pant is purchased and oxygen sales potential is neglected. The best case obtained is when both gases sales are considered and the owner already operates the PV plant, with the IRR being around 10% and the payback period of 8.4 years.

Comparing these values obtained with the scenario where gases are consumed in real time (even considering the hydrogen price 2 € lower) shown in figure 51, it can be seen a significant difference in the economic feasibility of the project. In fact, for the proprietary PV, with both gases being sold, the IRR is 28% with a payback period of just 3.5 years. Hence, the total investment project reaches a breakeven point in half the time, compared to the same case when considering compression and storage costs (figure 50). Even for the worst economic case, where only $H_2$ is being sold and the PV has yet to be purchased, the IRR is around 4.6% and the payback period is 12.8 years, which is a significant improvement compared to the estimated 18 years for the homologous conservative scenario.

In conclusion, all these calculations performed are merely rough estimations to analyse the feasibility of implementing an electrolyzer plant considering all different scenarios. The major highlight which can be drawn from such analysis is the impact of selling the co-produced oxygen, as well as its market price considered. Note that for the oxygen price, a very conservative price of 0.7 €/kg was considered, which is an average for all industries studied throughout this paper. If the oxygen was only to be sold for medical purposes, which has a clearly higher market price, the economic sensitivity would be even more attractive. On another point, compression and storage costs are also key to achieve economic viability, and should be the major focus of improvement for future scale up of such plants. Ultimately, is has been proven that the hydrogen price has little impact on the economic analysis when compared to the oxygen, which accentuates the tremendous potential of the oxygen market.

# 4 CONCLUSIONS

In conclusion, the major contributes of this work are not only the feasibility study of a solar powered electrolysis plant but mainly a thorough analysis on the most prominent locations in Portugal for the implementation of such plants. Industrial Hydrogen consumers were quantified, namely the oil refining sector, steel production and its future use in Integrated Combined Cycle Power plants. In addition, the key insight of this study was to evaluate the main oxygen consumers in the market, as well as the economic impact of reselling by-product oxygen of water electrolysis process.

Industrial oxygen has the highest oxygen demand in Portugal, with special focus in the glass industry, the major oxygen consumer. However, industrial oxygen market prices are considerably low compared to the medical oxygen market. In fact, current industrial oxygen cost might vary from 100 € up to 200 € per tonne, whereas medical oxygen has significant higher values (up to 8800 €/tonne for the B05 cylinders). Liquid bulk medical oxygen was estimated to represent a cost of 0.68 €/kg, with pressurized oxygen vessels reaching an average price of 2.38 €/kg for the B50 size and 8.8 €/kg for the B05 cylinders.

Several locations have shown to be particular promising for the instalment of green hydrogen production plants. Firstly, Sines, has tremendous opportunities for some reasons worth mentioning. The oil refining plant in Sines was estimated to have an annual demand of around 86 000 tonnes of $H_2$ for hydrotreatment and hydrocracking treatments. Being located in the southern region of Portugal, the solar potential for powering electrolysis is immense. However, future PV panels must be installed in order to reach the target of 2 GW electrolysis capacity by 2030. In fact, the current solar installed capacity in Sines is none, as shown in the 3D Maps obtained. Moreover, the possibility of exporting hydrogen both via maritime or overland routes to Europe is also a major advantage, as well as the current hydrogen consumption in the existing oil refining plant (sector with the highest industrial hydrogen demand). In terms of possible oxygen consumers in such location, the wastewater treatment stands out. In Portugal, a total demand of around 28 044 tonnes of $O_2$ per year was assumed for sludge treatment processes, with an estimation value of 1.78 tonnes of $O_2$/year per habitant/km$^2$ used for calculation purposes. Thus, for the region of Sines, 120 tonnes of $O_2$ can be consumed each year. For other oxygen consumers to benefit from an electrolysis plant in such location, oxygen transportation costs must be considered.

Other locations worth mentioning for the installation of electrolyzers are Figueira da Foz and Porto, as it can be seen from the 3D maps presented. Being located in the coastline of Portugal, such locations can leverage from maritime products importation and exportation as well as water abundancy for the water electrolysis process. In terms of industrial consumers of hydrogen and by-product oxygen, there is also strong potential in these locations.

Figueira da Foz has the largest papermaking industry in Portugal (total installed production capacity of 1.3 million tonnes of paper annually) and is also a considerable oxygen consumer for the glass industry (1 installed glass factory). Based on calculations, Figueira da Foz would require 61 650 tonnes of $O_2$/ year for the pulp industry and 100 000 tonnes of $O_2$/ year for glass production. As for the hydrogen application, the “Lares” natural gas combined cycle powerplant is the most evident future consumer, with an estimative demand of 11 724 tonnes of $H_2$.

Porto has also considerable medical and industrial oxygen consumption potential. In terms of medical oxygen, Porto is a sizeable consumer (1780 tonnes of $O_2$/year), only behind Portugal´s capital city, Lisbon (2957 tonnes of $O_2$/year). As for the industrial oxygen applications, the glass industry (existing factory in Vila Nova de Gaia) is a possible alternative, with a demand for 100 000 tonnes of $O_2$/year. The steel industry in Porto would also require around 15 000 tonnes of $O_2$/year in addition to 2 948 tonnes of $H_2$/year. Besides, Porto is the second district with the highest population density in Portugal, and consequently significant oxygen demand for wastewater treatment industry (9280 tonnes of $O_2$/year), according to the correlations performed in this study. Furthermore, there are some other relevant future hydrogen consumers worth mentioning. Such location could leverage from CaetanoBus hydrogen fuel cells technology, which is developing buses with 5 hydrogen tanks, with a total maximum capacity of 37.5 kg, and a 60 kW fuel cell. With a targeted annual production of 100 $H_2$ buses, it would represent a total of 3750 kg of hydrogen base consumption plus investing in recharging points. The combined cycle powerplant "Tapada do Outeiro" can also become a significant hydrogen consumer, reaching a demand of 14 052 tonnes of $H_2$.

Marinha Grande has also proven to be a promising location, since it has the highest installed capacity in Portugal of glass production (half of the total estimated production capacity, with 3 existing factories), which represent an oxygen consumption of 300 000 tonnes per year.

The table presented in Appendix A also represents a crucial part of the work carried out, describing the distribution of renewable energy sources in Portugal, as well the oxygen consumption by district for the medical and wastewater industry.

Finally, the diagram below shows a generic overview of all existing technologies to obtain both hydrogen and oxygen, as well as the several applications of both gases which were addressed in this paper. Note that some of these applications were thoroughly characterized and quantified, whereas others where just described in a more generic manner, for not being present in Portugal in impactful quantities.

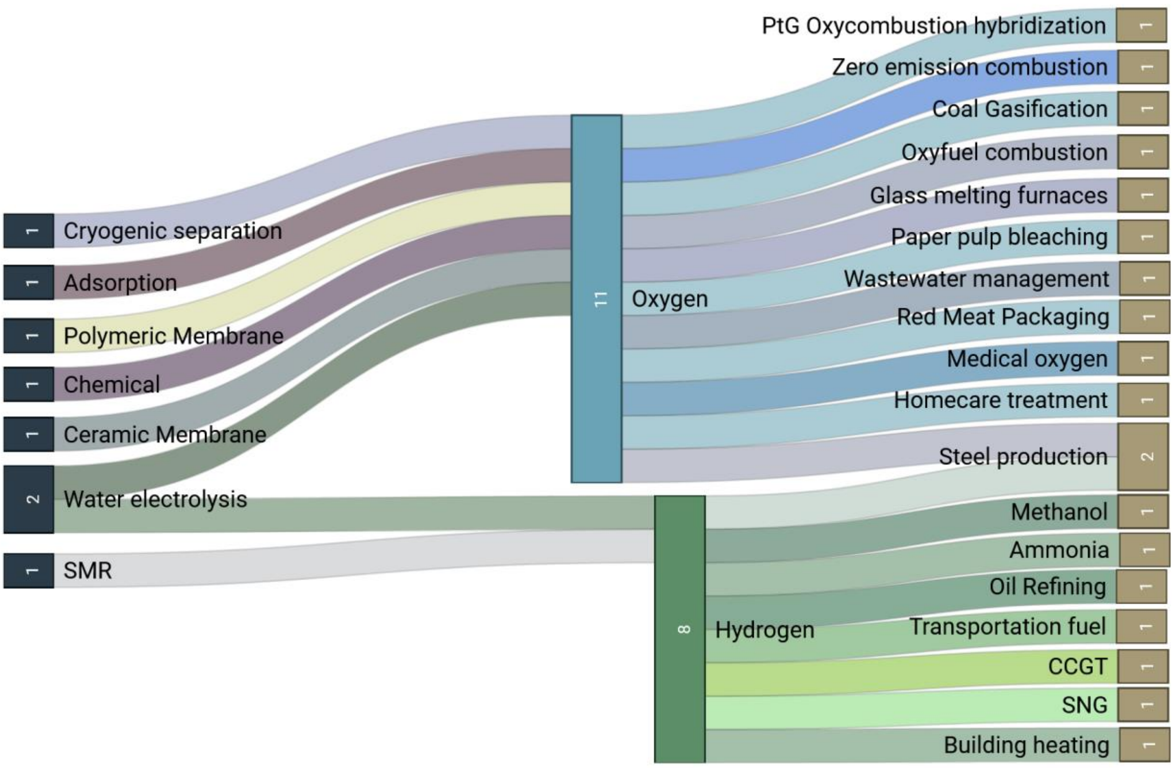


Figure 52 – Generic overview of hydrogen and oxygen applications

A continuous focus should be given to research and development in order to achieve feasibility of the capital-intensive alternative technologies for oxygen production, namely ceramic membranes that, together with electrolysis, will definitely play a key role in the near future.

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# APPENDICES

## Appendix A – 3D Map Excel Sheet

Data collected for Solar PV (MW), Wind Energy (MW), Hospitals (Oxygen consumption) and Wastewater Treatment (Oxygen consumption) [41], [61], [72]

| **Distrito** | **Conselho** | **Solar PV (MW)** [72] | **Wind (MW)** [72] | **Medical Oxygen (tonnes $O_2$/year)** [61] | **Wastewater Treatment (tonnes $O_2$/year)** [41] |
|---|---|---|---|---|---|
| Lisboa | Torres Vedras | | 117,9 | | |
| Leiria | Caldas da Rainha | | 10 | | |
| Porto | Póvoa de Varzim | | 2 | | |
| Vila Real | Vila Real | | 59,7 | | 235 |
| Braga | Vila Nova de Famalicão | 2,4 | | | |
| Setúbal | Santiago do Cacém | 12 | | | |
| Santarém | Santarém | | | | 185 |
| Leiria | Pombal | | 20 | 99 | |
| Porto | Amarante | | 37,6 | 111 | |
| Santarém | Mação | | 25,9 | | |
| Braga | Fafe | | 106 | | |
| Porto | Penafiel | | 10,8 | | |
| Viseu | Viseu | | 63,3 | | 341 |
| Lisboa | Alenquer | | 28 | | |
| Coimbra | Montemor-o-Velho | 2 | | | |
| Viseu | Mangualde | 0,1747 | | | |
| Bragança | Torre de Moncorvo | | 8 | | |
| Guarda | Celorico da Beira | | 72,1 | | |
| Guarda | Guarda | | 194,7 | | 98 |
| Braga | Braga | 0,1199 | | | 1769 |
| Viana do Castelo | Viana do Castelo | | 50,6 | | 472 |
| Vila Real | Vila Pouca de Aguiar | | 86,3 | | |
| Setúbal | Montijo | 23,21 | | | |
| Braga | Celorico de Basto | | 16,2 | | |
| Madeira | Machico | | 0,9 | | |
| Açores - São Miguel | Povoação | | 9 | | |

| | | | | | |
|---|---|---|---|---|---|
| Vila Real | Valpaços | | 165,6 | | |
| Viana do Castelo | Paredes de Coura | | | | |
| Açores - Terceira | Praia da Vitória | | 12,6 | | |
| Lisboa | Sintra | 2 | 6 | | |
| Castelo Branco | Penamacor | | 143,8 | | |
| Guarda | Sabugal | | 16,5 | | |
| Santarém | Ferreira do Zêzere | 0,4 | | | |
| Vila Real | Chaves | | 3,2 | | |
| Porto | Maia | 0,01 | | | |
| Lisboa | Lisboa | 0,05352 | | 2957 | 9044 |
| Açores - São Miguel | Ponta Delgada | | | | 519 |
| Bragança | Macedo de Cavaleiros | | 72 | | |
| Portalegre | Portalegre | | 8,2 | | 89 |
| Aveiro | Arouca | | 41,3 | | |
| Beja | Beja | | | | 52 |
| Faro | Albufeira | 6 | | | |
| Santarém | Ourém | | 22 | | |
| Lisboa | Cascais | 4 | | | |
| Setúbal | Alcácer do Sal | 7,2 | | | |
| Castelo Branco | Fundão | | 114 | | |
| Castelo Branco | Castelo Branco | 0,864 | 8 | | 64 |
| Santarém | Alcanena | 7,76 | | | |
| Faro | Silves | 14,43 | 6 | | |
| Leiria | Porto de Mós | | 98,3 | | |
| Beja | Mértola | 4,43 | 43,7 | | |
| Santarém | Rio Maior | | 121 | | |
| Setúbal | Alcochete | | | | |
| Faro | Alcoutim | 4,671 | | | |
| Viseu | Moimenta da Beira | | 165,2 | | |
| Setúbal | Seixal | 18,8 | | | |
| Beja | Almodôvar | 9,5 | 30,7 | | |
| Guarda | Trancoso | | 135,5 | | |
| Beja | Serpa | 11 | | | |
| Viseu | Armamar | | 253,2 | | |
| Porto | Porto | | 0,6 | 1780 | 9280 |
| Santarém | Tomar | 2,3 | | 111 | |
| Bragança | Bragança | | 0,8 | | 51 |

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|---|---|---|---|---|---|
| Coimbra | Soure | | 22 | | |
| Faro | Monchique | | 31,8 | | |
| Castelo Branco | Vila Velha de Ródão | | 2 | | |
| Beja | Ferreira do Alentejo | 34,5 | | | |
| Lisboa | Oeiras | 0,56 | | | |
| Lisboa | Cadaval | | 12 | | |
| Coimbra | Figueira da Foz | | 6 | | |
| Viseu | Vila Nova de Paiva | | 38 | | |
| Lisboa | Vila Franca de Xira | 2 | 19 | | |
| Viseu | Cinfães | | 95,2 | | |
| Porto | Marco de Canaveses | | 3,34 | | |
| Faro | Aljezur | | 34 | | |
| Viseu | Mortágua | | 32 | | |
| Açores - Santa Maria | Vila do Porto | | 1,5 | | |
| Coimbra | Coimbra | | 22,6 | 1261 | 747 |
| Faro | Loulé | 10,046 | | | |
| Viseu | Castro Daire | | 244,8 | | |
| Leiria | Alvaiázere | | 18 | | |
| Vila Real | Boticas | | 55,7 | | |
| Vila Real | Ribeira de Pena | | 44,4 | | |
| Viana do Castelo | Melgaço | | 263,5 | | |
| Porto | Trofa | 2 | | | |
| Coimbra | Góis | | 22,1 | | |
| Castelo Branco | Oleiros | | 44,1 | | |
| Castelo Branco | Proença-a-Nova | | 169 | | |
| Guarda | Seia | | 36,1 | | |
| Faro | Portimão | 2,61 | | | |
| Leiria | Ansião | | 6 | | |
| Beja | Moura | 59,8 | | | |
| Leiria | Leiria | | | | 394 |
| Coimbra | Cantanhede | | 9 | 1 | |
| Porto | Baião | | 33,9 | | |
| Coimbra | Arganil | | 275,4 | | |
| Viana do Castelo | Caminha | | 46,7 | | |
| Braga | Vieira do Minho | | 25,3 | | |

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|---|---|---|---|---|---|
| Coimbra | Condeixa-a-Nova | 2,4 | | | |
| Viseu | Resende | | 34 | | |
| Aveiro | Espinho | 0,1166 | | | |
| Viseu | Penalva do Castelo | | | | |
| Viseu | Penedono | | 4 | | |
| Lisboa | Loures | 16,445 | 56,2 | | |
| Aveiro | Ovar | 3,198 | | 3 | |
| Aveiro | Aveiro | 0,094 | | | 706 |
| Viseu | Oliveira de Frades | | 90 | | |
| Madeira | Calheta | | 11,1 | | |
| Évora | Estremoz | 11,185 | | | |
| Porto | Vila do Conde | 0,01 | | 10 | |
| Porto | Vila Nova de Gaia | 0,162 | | | |
| Aveiro | Santa Maria da Feira | | | 136 | |
| Lisboa | Arruda dos Vinhos | | 7,8 | | |
| Porto | Paços de Ferreira | 5,8 | | | |
| Lisboa | Lourinhã | | 50,5 | | |
| Vila Real | Mondim de Basto | | 53,5 | | |
| Leiria | Peniche | | 21,71 | | |
| Aveiro | Estarreja | 2,48 | | | |
| Viseu | Lamego | | 65,5 | | |
| Bragança | Mogadouro | | 4 | | |
| Lisboa | Mafra | | 25,55 | | |
| Évora | Évora | 50,334 | | | 71 |
| Viseu | São Pedro do Sul | | 40 | | |
| Faro | Lagos | 2,3 | 56 | | |
| Faro | Vila do Bispo | | 30 | | |
| Viseu | Tondela | | 29,9 | | |
| Leiria | Batalha | | 32,5 | | |
| Santarém | Coruche | 17,8 | | | |
| Açores - São Jorge | Calheta | | 1,8 | | |
| Madeira | São Vicente | | 9,3 | | |
| Faro | Tavira | 0,517 | 66,7 | | |
| Castelo Branco | Sertã | | 36,1 | | |
| Évora | Montemor-o-Novo | 2,462 | | | |

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|---|---|---|---|---|---|
| Coimbra | Pampilhosa da Serra | | 118 | | |
| Vila Real | Montalegre | 0,22 | 194,6 | | |
| Açores - Pico | Lajes do Pico | | 2,4 | | |
| Viana do Castelo | Vila Nova de Cerveira | | 10 | | |
| Madeira | Ponta do Sol | 9,2 | 24,92 | | |
| Açores - Faial | Horta | | 4,25 | | |
| Santarém | Chamusca | 1,455 | | | |
| Coimbra | Penacova | | 46,8 | | |
| Coimbra | Lousã | | 95 | | |
| Leiria | Castanheira de Pera | | 55,2 | | |
| Aveiro | Sever do Vouga | | 0,8 | | |
| Beja | Ourique | 46,13 | | | |
| Faro | Faro | 3,226 | | | 536 |
| Coimbra | Penela | | 33,71 | | |
| Porto | Matosinhos | 1,209 | | | |
| Viseu | Tarouca | | 4 | | |
| Açores - Flores | Lajes das Flores | | 0,6 | | |
| Leiria | Nazaré | | 14 | | |
| Bragança | Freixo de Espada à Cinta | 0,11 | | | |
| Santarém | Salvaterra de Magos | 24 | | | |
| Madeira | Funchal | | | | 2433 |
| Aveiro | Ílhavo | 0,391 | | | |
| Setúbal | Setúbal | 2,29 | | | 892 |
| Açores - Graciosa | Santa Cruz da Graciosa | 1 | 6,3 | | |
| Coimbra | Miranda do Corvo | | 58,6 | | |
| Évora | Vendas Novas | 13,2 | | | |
| Setúbal | Palmela | 4,007 | | | |
| Portalegre | Castelo de Vide | 24 | | | |
| Setúbal | Sines | | 18,7 | | 120 |
| Porto Santo | Porto Santo | 2 | | | |
| Lisboa | Sobral de Monte Agraço | 0,2 | 41,5 | | |